

AD-A142 718 CHEMICAL CHARACTERIZATION AND TOXICOLOGIC EVALUATION OF 1/1
AIRBORNE MIXTURES. (U) OAK RIDGE NATIONAL LAB TN
R A JENKINS ET AL. NOV 83 ORNL-TM-9196

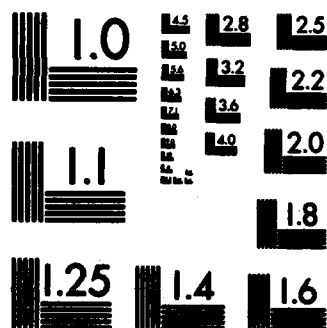
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MARTIN MARIETTA

AD-A142 718

**Chemical Characterization and
Toxicologic Evaluation of
Airborne Mixtures**

**CHEMICAL AND PHYSICAL
CHARACTERIZATION OF
DIESEL FUEL SMOKE**

R. A. Jenkins
R. W. Holmberg
J. S. Wike
J. H. Moneyhun
R. S. Brazell

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U.S. ARMY MEDICAL BIOENGINEERING RESEARCH AND
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Diesel fuel no. 2 (DF2) used in the vehicle engine exhaust smoke system (VESS) has been chemically and physically characterized. A battery of fractionation procedures was used, including elemental analysis, inductively coupled plasma, UV/visible and infrared spectrometrys, high performance liquid chromatography (HPLC), gas chromatography and GC/MS. The best overall characterization was provided by HPLC, which yielded four major fractions (saturated hydrocarbons, 70 percent; substituted benzenes, 16 percent; 2-ring aromatics, (Continued on reverse)		

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19. hydrocarbons	particles	tracer
infrared spectrometry	petroleum	UV spectrometry
liquid chromatography	phenanthrene	vapor
military	smoke	VEESS
obscurant	spectrometry	

20. 12 percent; and 3-ring aromatics, 2 percent) and one minor fraction (polar aromatics, 0.2 percent). These fractions were further analyzed by GC/MS. No single component accounted for more than about one percent of the DF2. The major effect of aerosolization of the DF2, in a generator designed to simulate the military deployment of VEES smoke, was partitioning of constituents between the vapor and the liquid particulate phase on the basis of their relative volatility. No significant levels of constituents not found in the unaerosolized DF2 were observed in the liquid phase of the smoke generated from it.

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Chemical Characterization and Toxicologic Evaluation of
Airborne Mixtures

CHEMICAL AND PHYSICAL CHARACTERIZATION OF DIESEL FUEL ~~SMOKE~~^{2c}

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EXECUTIVE SUMMARY

The purposes of the work described in this report were threefold: (1) to describe the chemistry of a diesel fuel smoke undergoing inhalation toxicology studies, (2) to define the diesel fuel used in the study to ascertain what chemical changes occur as a result of aerosolization, and (3) to provide a data base with which to compare other fuels for the purpose of future risk assessment studies. The fuel used was a reference diesel fuel No. 2 designed for use in compliance testing of motor vehicles. The physical characteristics of the fuel, including density, kinematic viscosity, flash point, particulate contamination, simulated distillation ranges, and accelerated stability were determined according to standard procedures. A comparison of the data obtained from tests performed in our laboratory with those of specifications provided by the EPA or Department of Defense indicated that the fuel used in the study was within normal specification range.

The chemical characterization of the diesel fuel and fuel smoke was designed to be sufficiently broad to be applicable to a variety of diesel fuels which may be employed in future tests and also be generally applicable to the analysis of condensed smokes. Therefore, a battery of testing procedures, including elemental analyses, Fourier transform infrared spectrometry, UV/visible spectrometry, high performance liquid chromatography (HPLC), and high resolution gas chromatography (GC) and GC/MS were employed. The hydrogen:carbon molar ratio for the fuel was 1.80:1. This was close to that predicted from the 70:30 aliphatics:aromatics ratio determined by HPLC. Sulfur (at 0.39 percent) was the most prevalent non-hydrocarbon element. Little evidence was obtained of trace metal contamination in the fuel. Barium, calcium, cadmium, copper, and lead were at levels between 0.1 and 0.01 ppm. UV/visible spectral analysis indicated a strong absorption band in the ultraviolet region. This absorption increased upon exposure of the fuel to light. Therefore, fuel was kept in the dark during storage periods. The infrared spectrum was characterized by strong absorptions for C-H stretching and bending. Very few other strong absorptions were noted.

Class fractionation of the diesel fuel by HPLC yielded one minor and four major fractions. These fractions were then subjected to GC and GC/MS for qualitative and quantitative analysis. The first fraction (approximately 70 percent of the fuel, by weight) consisted predominantly of straight and branched chains saturated hydrocarbons, present at maximum concentrations of 10-12 mg per g fuel. The second fraction (approximately 16 percent of the fuel) consisted of alkyl substituted benzene compounds. These were present at maximum concentrations of 1 - 2.5 mg per g fuel. The third fraction (approximately 12 percent of the fuel) was composed predominantly of two-ring aromatics, including naphthalene, alkylated naphthalenes, alkylated biphenyls, and small amounts of thiophenes. The most prevalent constituents were present at concentrations of 5-10 mg per g fuel. The fourth fraction (approximately 2 percent of the fuel) consisted of predominantly three-ring hydrocarbons, including fluorene, alkylated fluorenes,

phenanthrene, and alkylated phenanthrenes. These were present at concentrations of 2-4 mg per g of fuel. A minor (0.2%), more polar fraction, contained alkyl substituted indoles, carbozoles, and alkyl substituted carbazoles. The most prevalent constituents in this fraction were present at concentrations of 40-90 micrograms per gram fuel. Benzo(a)pyrene was present in the fuel at a concentration of approximately 70 ng per mL.

The single greatest effect of the high temperature aerosolization procedure was to partition the components of the diesel fuel between vapor and liquid phases. This occurs because the obscurant cloud is an evaporation-condensation aerosol which, when generated, undergoes a large dilution simultaneously with condensation. Many of the more volatile constituents in the fuel have significant vapor pressures at ambient temperatures and thus partition themselves between the vapor and particle phases. Further experiments indicated that, as the smoke becomes more dilute, a greater fraction of the fuel remains uncondensed. At the concentrations used in the study, the fraction of fuel remaining in the vapor phase ranged between 7 and 20 percent. Comparison of specific constituent concentrations in the various fractions of the particle phase of the smoke with those reported for the fuel itself indicated a lowered concentration of both one-ring aromatics and more volatile straight chain saturated hydrocarbons in the smoke particles. These compounds were identified in the vapor phase of the smoke. Concentrations of other constituents in the fuel and smoke were generally within the range of experimental uncertainty of each other. No significant levels of constituents not present in the original fuel were observed in the liquid phase of the smoke. Only traces of carbon monoxide (CO) and oxides of nitrogen (NO_x) were present in the vapor phase.

Scoping studies were conducted by adding oxygen to the smoke generator carrier gas to better simulate the chemical environment existing inside the exhaust manifold of an armored vehicle. Results obtained suggested that field generated smoke would contain more NO_x and CO, and that about 25 percent of the aliphatic constituents of the particle phase would be depleted due to combustion. The smoke changed color and odor.

FOREWORD

In conducting the research described in this report, the investigators adhered to the "Guide for Laboratory Animal facilities and Care," as promulgated by the Committee on the Guide for Laboratory Animal Facilities and Care of the Institute of Laboratory Animal Resources, National Academy of Sciences-National Research Council.

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INTRODUCTION

The military has shown renewed interest in the use of smokes and obscurants for screening purposes in warfare. This, coupled with the present-day concerns for environmental and occupational exposure safety has prompted the Army to investigate the risks associated with passive accidental exposure to these smokes. As part of this program, the Department of Defense is supporting an investigation of the inhalation toxicology of one of these obscurants. In this case, smoke is produced by diesel powered vehicles from diesel fuel with a system designated by the acronym VEES (Vehicle Engine Exhaust Smoke System.) Briefly, the same fuel that powers the vehicle is pumped into the exhaust manifold immediately downstream of the engine. The fuel vaporizes and the vapors are carried through the exhaust system and forcibly ejected along with the normal exhaust gases into the air. The vapors condense to form an aerosol cloud which is used for screening.

The size and cost of a large vehicle such as a tank, as well as the amount of aerosol which the VEES system produces, precluded its direct use in a laboratory scale inhalation exposure. Therefore, we have undertaken a study employing exposures to a diesel fuel based smoke generated under similar conditions but on a much smaller scale. The purpose of the work described in this report was (1) to describe the chemistry of the smoke to which the animals undergoing inhalation exposure are exposed and (2) to define the diesel fuel to ascertain what chemical changes occur as a result of aerosolization and to provide a data base with which to compare other fuels for the purposes of future risk assessment studies.

PHYSICAL CHARACTERISTICS OF THE DIESEL FUEL

Diesel fuel is a complex mixture of aromatic and aliphatic hydrocarbons containing small quantities of additives. Diesel fuel may be obtained directly from the fractional distillation of crude petroleum (straight run distillates), or from catalytic hydrogenation of the petroleum. In any case, diesel fuel usually corresponds to the crude petroleum fraction boiling approximately in the range of 160 to 370°C. Much literature exists on the characteristics of diesel fuel - predominantly from a physical characteristics standpoint. Detailed chemical characterization studies have been limited.

The fuel used in this study was a Diesel Fuel No. 2 (DF-2) and was obtained from Phillips Petroleum Company. It is a reference fuel designed for use in compliance testing of motor vehicles. The fuel was not chosen because of any particular toxicological relevance, since little comparative toxicity data exists on diesel fuels. In addition, a priori estimation of the toxicity would require knowledge of the exact, detailed chemical composition of the fuel. Rather, choice of the fuel represented an attempt to use a relatively well characterized, "average" diesel fuel. Enough fuel was procured so as to be assured of an uninterrupted supply throughout the exposures.

The fuel was received in September, 1980 in 55-gallon drums and stored refrigerated at 4°C until use. When an individual barrel was opened for use, it was warmed to approximately 20°C, tumbled for two hours, and aliquotted into 5-gallon fuel safety cans. The safety cans had been previously washed with hexane, ethanol, detergent and water, and ethanol, sequentially, to remove traces of residual oil or fuel. The filled cans were also stored refrigerated until immediately prior to use. For the inhalation exposures, no fuel was allowed to remain at room temperature for more than one month.

METHODS

Density determinations were performed at 25°C by weighing a specified volume of fuel. Kinematic viscosities were determined at both 40°C and 25°C according to ASTM procedure D445-53T. Flash point determination was performed according to ASTM Procedure D93-58T. Particulate contamination of the diesel fuel was determined by filtering a one-half liter quantity of the fuel through a one-micrometer pore size glass fiber filter (Gelman Sciences, Inc.). The weight increase of the filter pad was taken to be the amount of particles present in the filtered volume. Simulated distillations were performed according to ASTM D2887-73. Accelerated stability testing was performed according to ASTM D2274-74. Refractive indices were determined on a refractometer.

RESULTS

In Table 1 are listed various physical tests and parameters for the diesel fuel used in this study, along with the manufacturer's specifications for that particular parameter and EPA or Department of Defense specification ranges for selected parameters. A comparison with tests performed in our laboratory indicates that the fuel used was within the normal specification range. Accelerated stability testing, performed after the fuel had been refrigerated approximately 12 months, indicated that the level of total insolubles was still well within the limits specified for diesel fuel. There were some differences between the distillation points measured at ORNL and those determined for the manufacturer's specification. These may be due to the fact that the ORNL procedure is not a true distillation but rather a gas chromatographic simulated distillation. However, the boiling points were well within specification limits.

CHEMICAL CHARACTERIZATION OF THE DIESEL FUEL

A "complete", exhaustive chemical characterization of the material used to generate the VEES smoke would involve considerable effort and resources and was beyond the scope of the project. The purpose of the work performed for this study was to develop a data base (1) with which to compare other diesel fuels, and (2) to provide for the determination

TABLE 1. PHYSICAL CHARACTERISTICS OF DIESEL FUEL #2 USED IN ORNL STUDY

Parameter	ORNL Determined Value	Manufacturer Specification	EPA Specification Range	Military Specifications CONUS (OCONUS)
Density at 25° g·mL ⁻¹	0.844	—	—	(.815-.860)
Viscosity at 40° centistokes at 25° centistokes	2.456 3.35	2.67	2.0 - 3.2	1.9 - 4.1 —
Flash Point °C minimum	74	78	54.4	52
Particulate Contamination, mg·L ⁻¹ , maximum	5	—	8	10
Distillation Range				
10% Point, °C	186 ^a	219 ^b	204-238 ^b	—
50% Point, °C	271	262	243-282	Report
90% Point, °C	320	298	288-321	338
Accelerated Stability total insolubles, mg per 100 mL, maximum	0.42	—	1.5	1.5
Refractive Index	1.4770	—	—	—

^aDetermined by simulated distillation, ASTM D2887-73

^bDetermined by actual distillation, ASTM D86-78

of the effects of aerosolization on the fuel. The chemical characterization was to be sufficiently broad to be applicable to a variety of diesel fuels and also be generally applicable to the analysis of condensed smokes. Ideally, the procedures had to be directed toward characterization of a large fraction of the total mass of fuel (as opposed to the determination of small quantities of additives) and had to be performed on a routine basis. Thus, rather than one particular analytical procedure being employed (such as high resolution gas chromatography), a battery of testing procedures was used to define the chemical composition of the diesel fuel.

METHODS

Carbon and hydrogen analyses were performed according to ASTM Procedure D3178-3. Elemental nitrogen determinations were performed by ASTM Procedure D-3179-73. Elemental bulk sulfur determinations were performed by ASTM Procedure D3177-75. Minor modifications of the methods were made in order to handle liquid petroleum samples. Trace metal determinations were conducted on dodecane solutions of the diesel fuel by inductively coupled plasma analysis. UV/visible spectra were obtained on a Cary 14 recording spectrophotometer or a Varian Model DMS 90 recording spectrophotometer. Diffuse reflectance Fourier Transform infrared spectra were obtained by spotting small portions of fuel onto potassium bromide powder. The mixture was then pressed into pellets and spectra taken on a Digilab Model FTS-20C FTIR Spectrometer.¹

High performance liquid chromatographic (HPLC) separations or fractionations of diesel fuel or dilute diesel fuel were performed on a semi-preparative scale 5-micrometer particle diameter silica column (two Altex Ultrasphere - Si columns in series). Usual injection size was 50 microliters. Aliphatic and aromatic constituents in the fuel were isocratically eluted with hexane at 1.1 mL per minute using a Laboratory Data Control HPLC Pump. The more polar constituents were eluted by changing the mobile phase to methylene chloride or a 50:50 methylene chloride:hexane mixture. Detection of fuel constituents was performed with either refractive index detection or UV detection at 254 nm. Benzo(a)pyrene analyses were performed by sequential HPLC analyses, as described elsewhere.²

Most gas chromatographic determinations of diesel fuel constituents were performed on a Hewlett Packard 5840A gas chromatograph. Two-microliter splitless injections were made onto either a 30-m, SE-52-coated, fused silica capillary column or 50-m OV-101-coated fused silica capillary column. Hydrogen was the carrier gas. The usual temperature program was: 2 minute hold at 50°C and then program at 2° per minute to 250°C. Quantitative determinations were performed by comparing peak areas with those of external standards. Mass spectral data were obtained with a Hewlett Packard 5895A GC/MS system equipped with a dual EI/CI source. EI source potential was 70 eV. Procedures for ammonia chemical ionization GC/MS have been described in detail elsewhere.³

RESULTS AND DISCUSSION

Analysis of the bulk elemental composition of the fuel provides a basis for the estimation of the relative levels of more polar constituents in the predominantly hydrocarbon matrix. For example, if nitrogen, oxygen, or sulfur levels are relatively high, substantial levels of more polar constituents are more likely to be present in the diesel fuel. Data for the CHNOS analyses are listed in Table 2. The level of sulfur (.39 percent) determined at ORNL was in good agreement with that provided by the manufacturer (.34 percent). The hydrogen:carbon molar ratio for the diesel fuel was 1.80. This is very close to what would be predicted based on the manufacturers specification of 71 percent aliphatic hydrocarbons and 29 percent aromatic hydrocarbons.

TABLE 2. BULK ELEMENTAL ANALYSIS OF DIESEL FUEL

Element	Mean Weight Per Cent
Carbon	86.8
Hydrogen	13.05
Nitrogen	0.01
Oxygen (by difference)	< 0.1
Sulfur	0.388

Determination of the trace element content of the fuel was difficult due to the predominantly hydrocarbon nature of the matrix. Attempts to determine approximately 20 elements including aluminum, silver, calcium, chromium, copper, magnesium, nickel, and lead were performed using inductively coupled plasma (ICP). Results of the determinations indicated that the levels for all of these elements were below the limit of accurate determination of the ICP (approximately 1 microgram per gram of fuel). Order-of-magnitude estimates of trace metal content based on the ratio of the emission intensities of the fuel samples and fuel samples spiked to 1 ppm of the element in question yielded the data found on Table 3. These data suggested that barium, calcium, cadmium, copper and lead were at levels above .01 ppm. All other elements tested were less than 0.01 ppm.

A UV/visible spectral scan of the diesel fuel and dilute diesel fuel are portrayed in Figure 1. The fuel itself is a slightly pale yellow color. The absorption spectrum of the fuel had few distinguishing features other than a strong absorption band in the UV region. This suggested that the yellow color observed was not from a particular species absorbing blue light in the visible region but rather a result of UV absorption tailing into the visible region. The diesel fuel tended to darken upon standing in room light. This was manifested as an increase in absorption of the near UV region (see below).

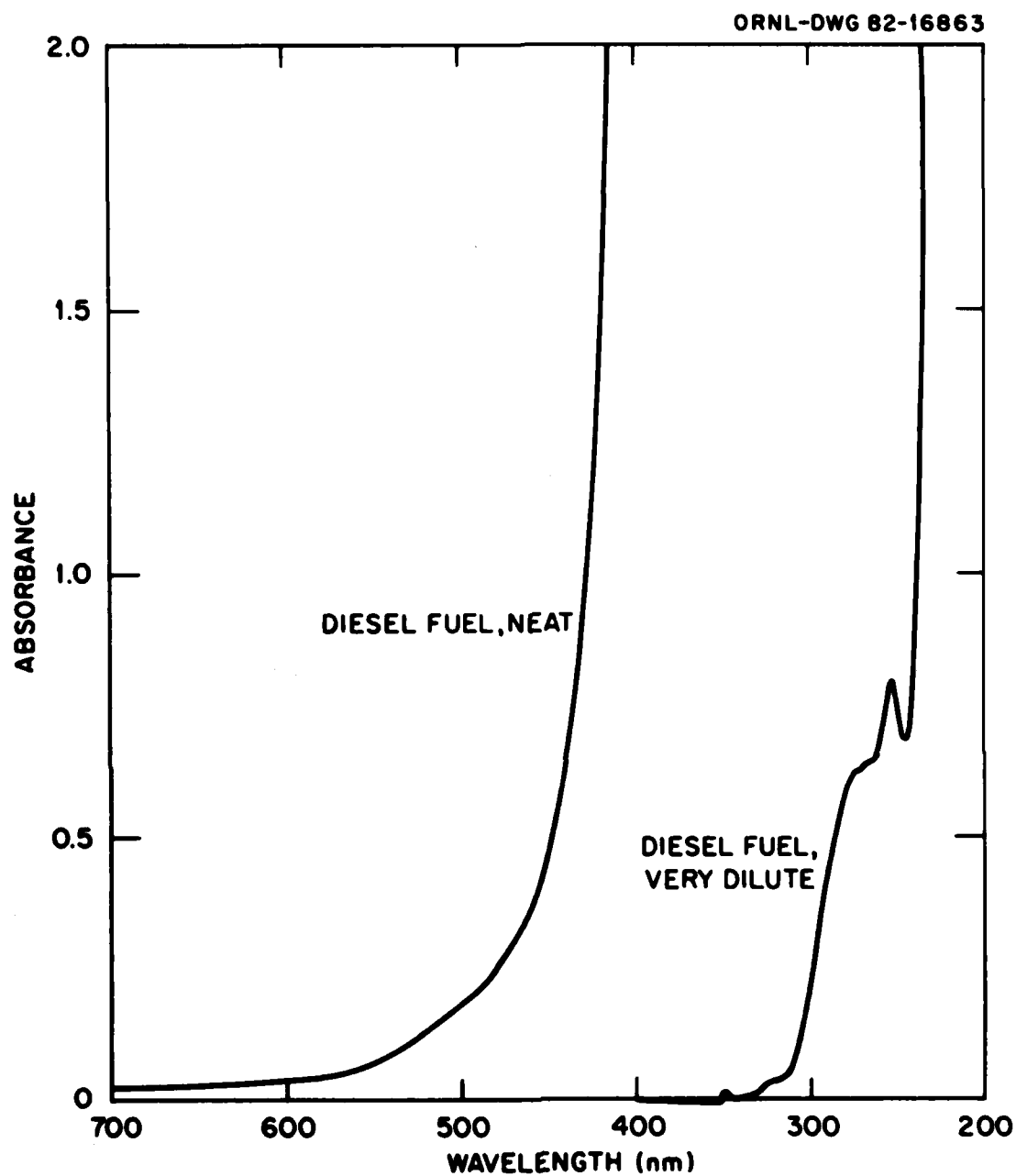


Figure 1. Ultra-Violet and Visible Spectra of Neat and Diluted Diesel Fuel

TABLE 3. ESTIMATED TRACE ELEMENT CONCENTRATIONS IN DIESEL FUEL

Element	Concentration, $\mu\text{g/mL}$
Ag	< .01
Al	< .01
B	< .01
Ba	0.01
Ca	0.1
Cd	0.01
Cr	< .01
Cu	0.1
Fe	< .01
Mg	< .01
Mn	< .01
Mo	< .01
Na	< .01
Ni	< .01
P	< .01
Pb	0.1
Si	< .01
Sn	< .01
Ti	< .01
V	< .01
Zn	< .01

Diffuse reflectance Fourier Transform Infrared Spectrometry (FTIR) provided the equivalent of a bulk chromophore characterization of the diesel fuel matrix. An FTIR spectrum is portrayed in Figure 2. The spectrum is characterized by very strong absorptions for C-H stretching and bending. There are minor absorptions due to carbon-carbon double bonds. Very few other strong absorptions were noted.

High performance liquid chromatography was used to chemically characterize the diesel fuel for three primary reasons. First, the HPLC measurement of the aromatic/aliphatic ratio of the fuel is inherently a more accurate measure of this universally accepted parameter because of HPLC's separation of specific compounds according to compound class type. Secondly, an HPLC chromatogram of the diesel fuel can provide for a rapid qualitative "fingerprint" the chemical nature of the fuel. Thirdly, use of a semi-preparative scale HPLC column can provide compound class fractions of the fuel for more lucid visualization of the particular components of given fractions. In Figure 3, an HPLC chromatogram of the diesel fuel used in the experiments is depicted. In order to determine the aromatics/aliphatics ratio of the fuel, initial structural identification of specific compounds in various fractions of the fuel was conducted (see below). Briefly, fraction A consisted of

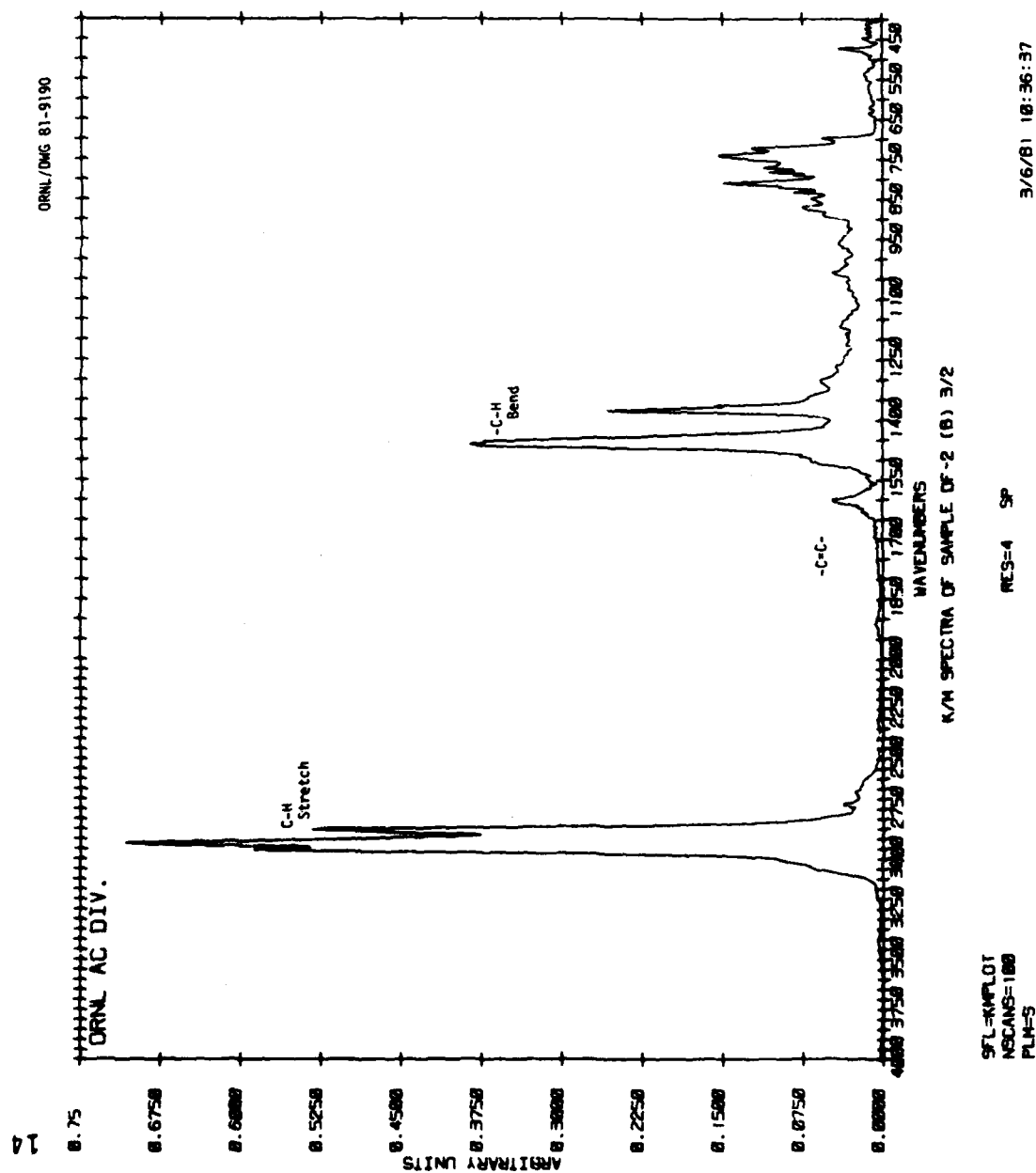


Figure 2. Diffuse Reflectance Fourier Transform Infrared Absorption Spectra of Phillips #2 Diesel Fuel

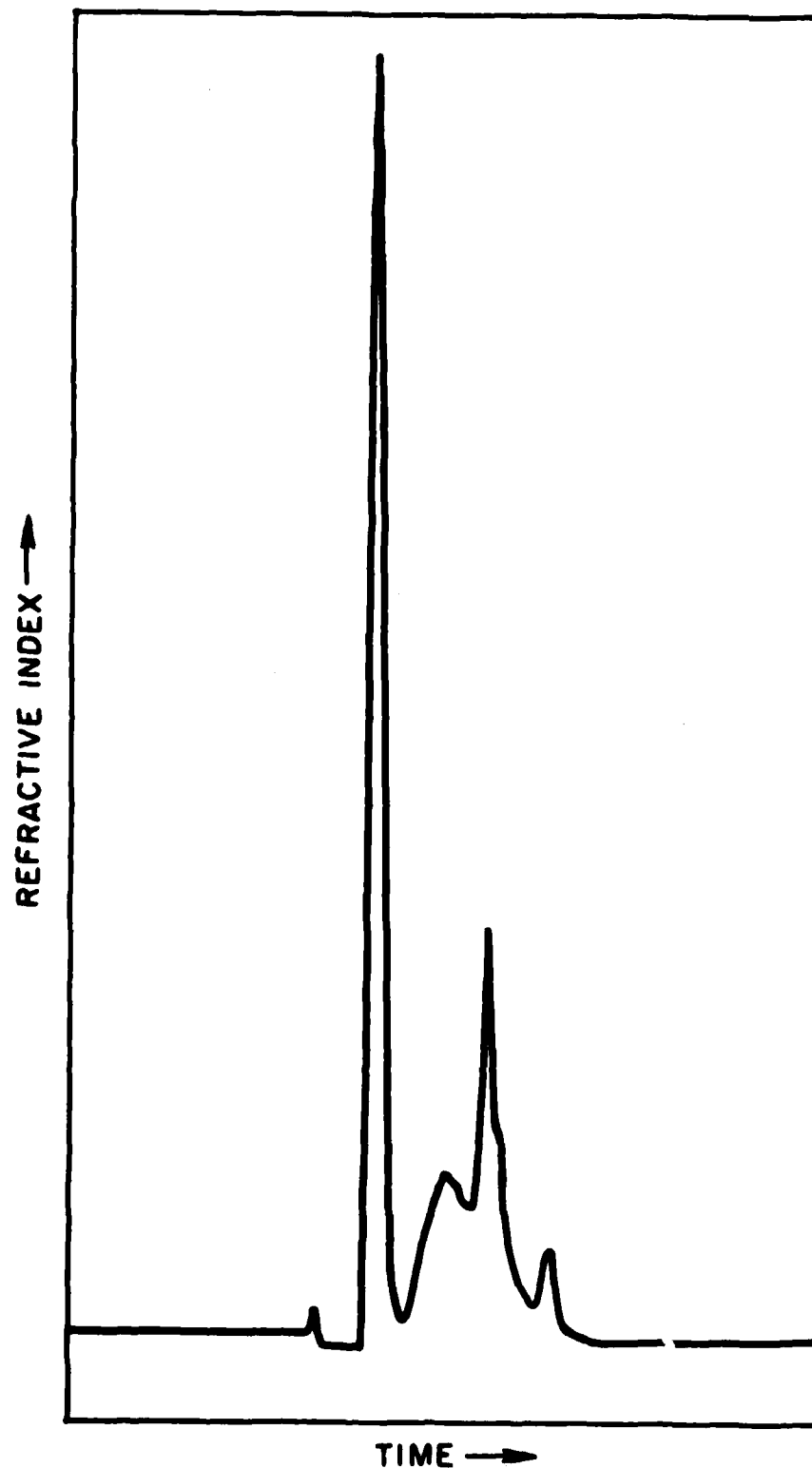


Figure 3. High Performance Liquid Chromatogram (HPLC) With Refractive Index Detection of Phillips #2 Diesel Fuel

straight and branched chain hydrocarbons. Fractions B, C, and D contained predominantly one, two, and three ring aromatics, respectively. Because of differences in specific refractive indices among various fuel constituents, standardization with compounds similar to those found in the fuel had to be performed. This was accomplished by choosing standard compounds which had specific refractive indices close to those of the constituents in each of the four major compound classes within the fuel. The compounds chosen for the standardization included dodecane, toluene, naphthalene, and 3,6-dimethylphenanthrene. The proportion of aromatic compounds in the fuel determined by this procedure yielded values very close to those obtained by independent tests (29.3 percent aromatics by HPLC at ORNL versus 30.5 percent by analysis supplied with the fuel). The aromatic fractions B, C, and D made up approximately 16, 12, and 2 percent (by weight) of the fuel, respectively.

As stated previously, HPLC can provide for a rapid qualitative comparison of the differences among various fuels being tested. For example, Figure 4 compares the HPLC chromatograms of two fuels examined during these experiments. The diesel fuel labeled VEES was that sampled during a field exercise at Smoke Week III. Comparison of the two chromatograms indicates that, even with this relatively crude approach, differences among the fuels can be clearly seen.

Because of the considerable complexity of the diesel fuel matrix, even high resolution gas chromatography on a fused silica capillary column can be insufficient for determining important but minor constituents in the fuel. For example, Figure 5 is a high resolution gas chromatogram of the diesel fuel. The predominant peaks in the chromatogram are the straight chain saturated hydrocarbons. However, it is clear that other constituents are present in smaller but significant amounts. In order to more lucidly visualize other, non-saturated hydrocarbons, the fuel was subjected to a tiered analytical scheme. In this case, the diesel fuel is first separated into class fractions by semi-preparative scale HPLC. The specific HPLC fractions were collected and reduced in volume to approximately 500 microliters in a manner so as to prevent loss of the more volatile constituents. An aliquot of the fuel fraction concentrate was then subjected to high resolution gas chromatographic separation. This is portrayed in Figure 6.

Figure 7 is a high resolution gas chromatogram of fraction A of the fuel. The most predominant peaks in the fraction - the straight chain saturated hydrocarbons - were identified using high resolution GC/MS and comparison of retention times of authentic standard compounds. The remaining constituents were tentatively identified as branched chain hydrocarbons. However, because of the similarity of the molecular fragmentation patterns, it was not possible to unambiguously identify other specific constituents within the fraction. Table 4 lists concentrations of the straight chain hydrocarbons in the fuel fraction A. Concentrations ranged upward to approximately 10 to 12 milligrams of n-C₁₇H₃₆ per gram of fuel. Comparison of peak

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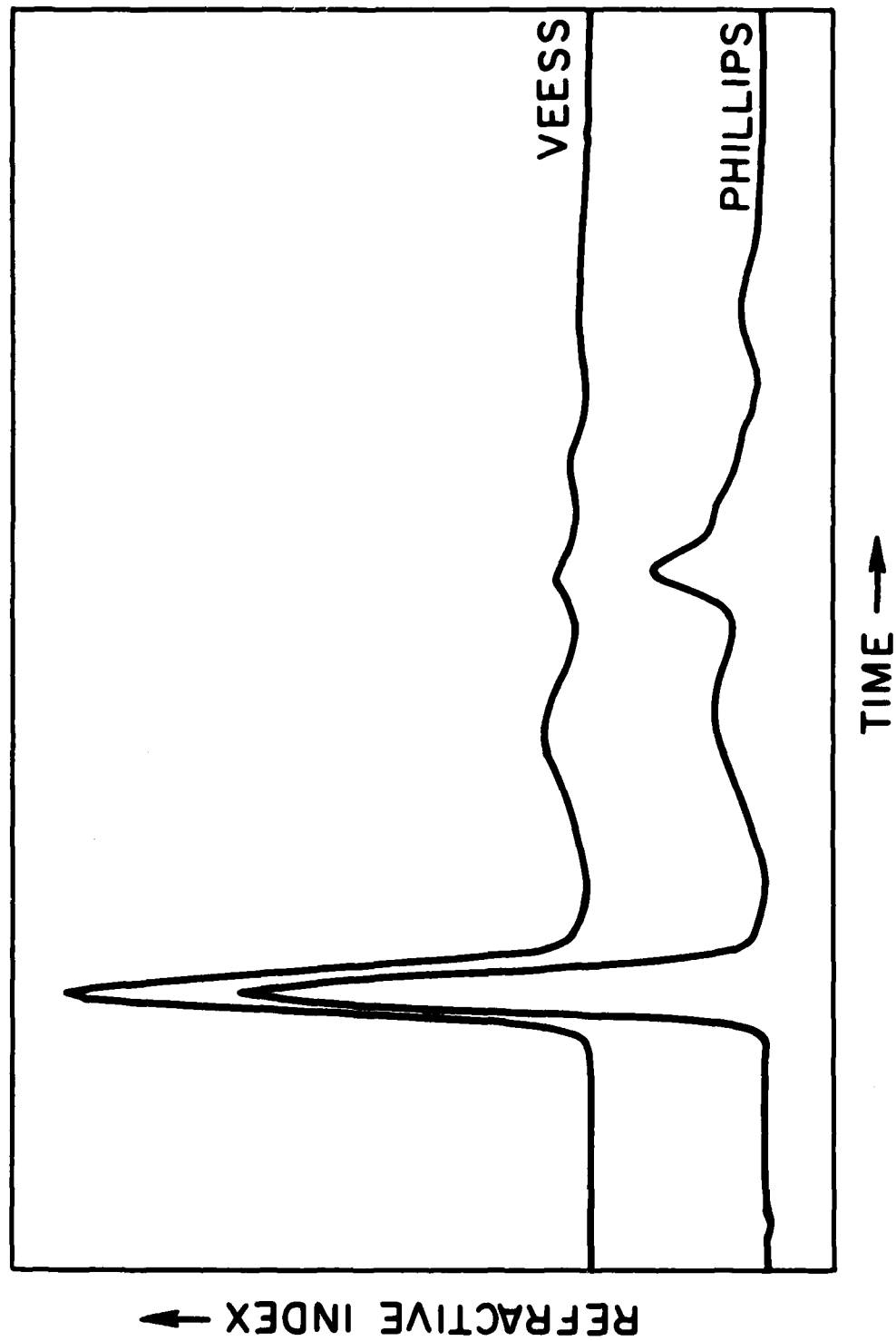


Figure 4. Comparison of HPLC Chromatograms of Diesel Fuel Used in Inhalation Exposures and That of Fuel Collected at Smoke Week III

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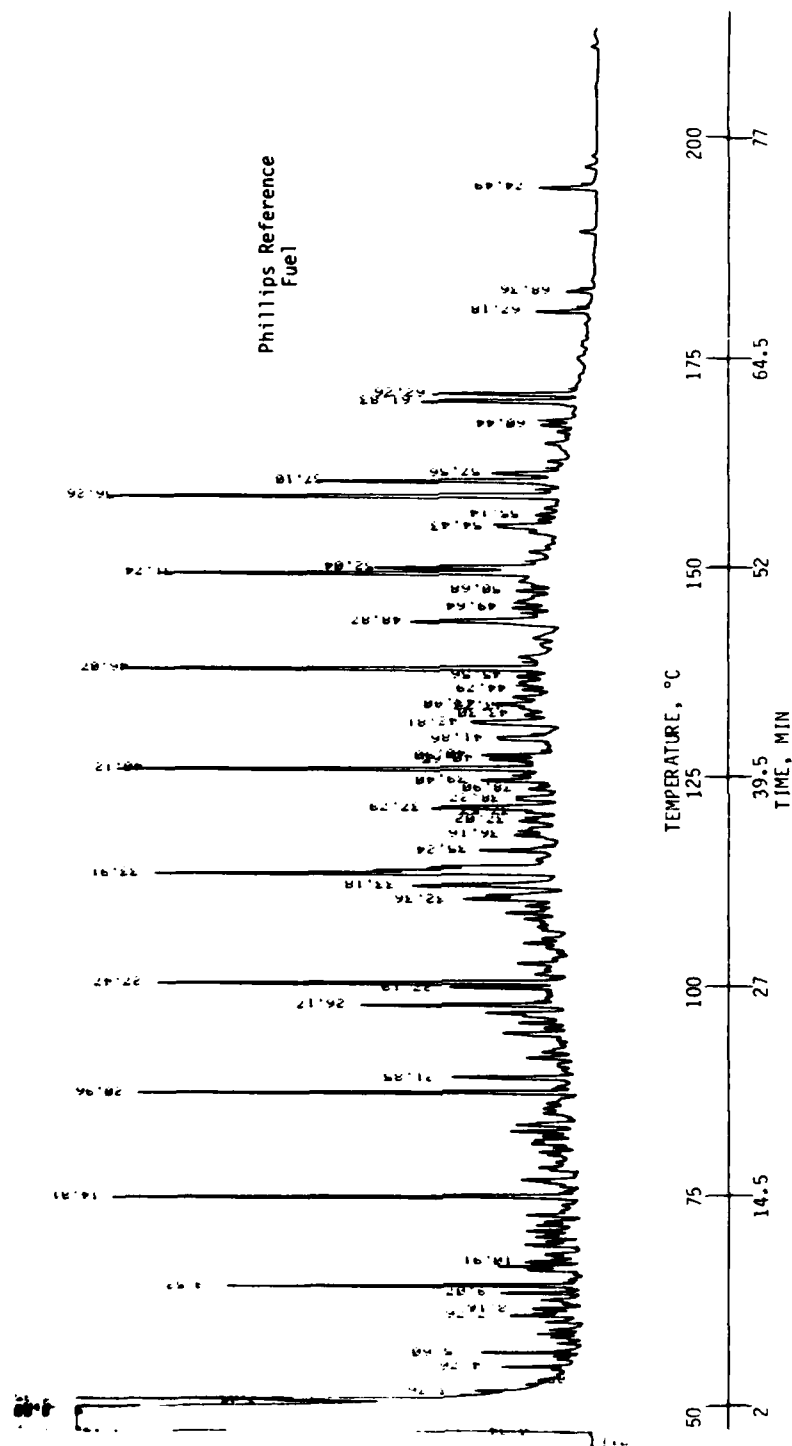


Figure 5. High Resolution Gas Chromatographic (GC) Profile of Diesel Fuel

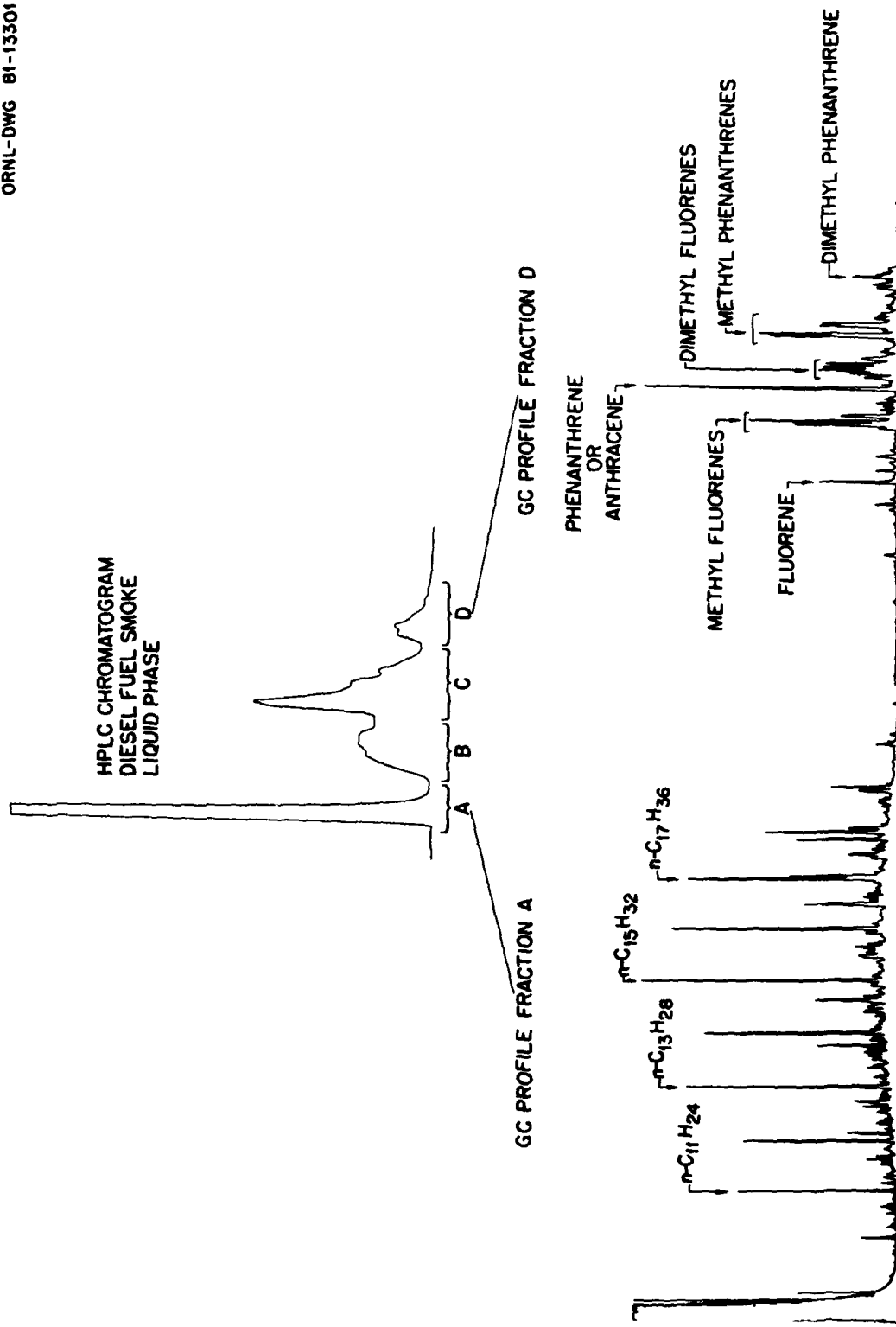


Figure 6. HPLC Fractionation of Diesel Fuel Followed by High Resolution GC Visualization of Individual Fractions

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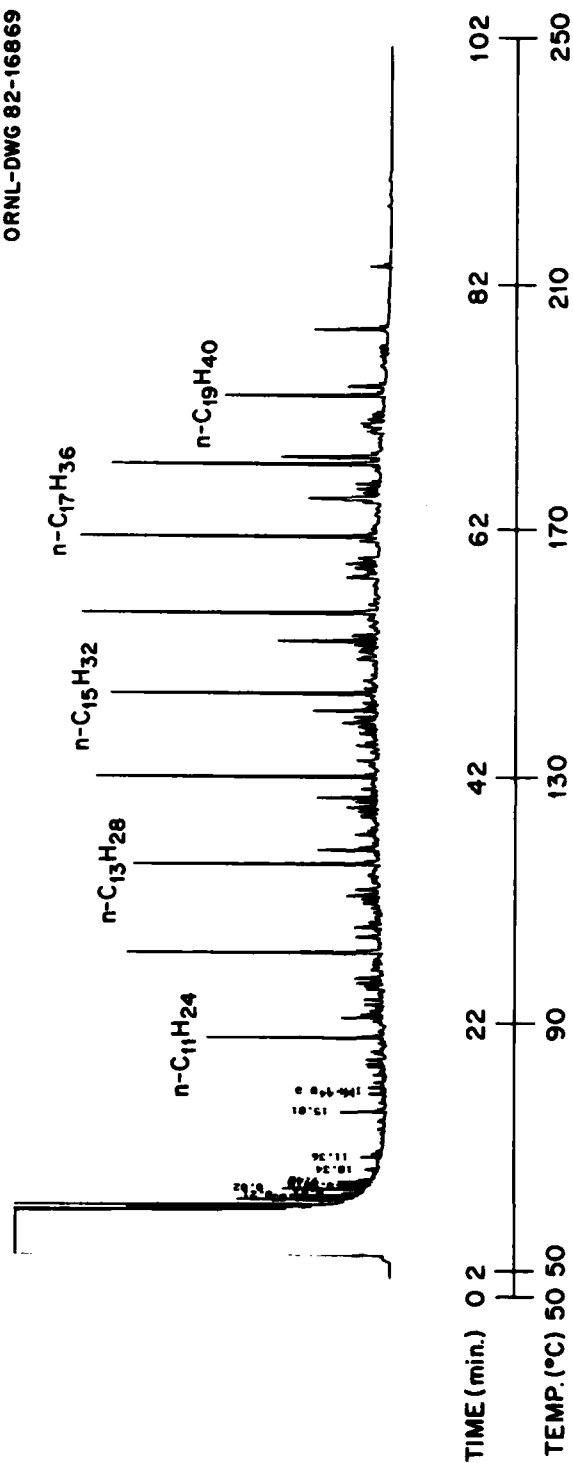


Figure 7. High Resolution GC Profile of the Aliphatic Fraction of Diesel Fuel

TABLE 4. CONCENTRATIONS OF SELECTED CONSTITUENTS
ALIPHATIC FRACTION OF DIESEL FUEL

Constituent	Concentration (mg/g fuel, mean \pm one standard deviation)
n-C ₉ H ₂₀	1.0 \pm 0.0
n-C ₁₀ H ₂₀	5.2 \pm 0.3
n-C ₁₁ H ₂₄	9.8 \pm 0.8
n-C ₁₂ H ₂₆	9.6 \pm 0.5
n-C ₁₃ H ₂₈	11 \pm 0.4
n-C ₁₄ H ₃₀	11 \pm 0.3
n-C ₁₅ H ₃₂	10 \pm 0.7
n-C ₁₆ H ₃₄	12 \pm 0.6
n-C ₁₇ H ₃₆	12 \pm 1.0
n-C ₁₈ H ₃₈	8.2 \pm 1.3
n-C ₁₉ H ₄₀	5.3 \pm 0.5
n-C ₂₀ H ₄₂	2.3 \pm 0.2

heights between the normal and branched chain hydrocarbons suggest that these constituents are present at approximately a factor of 5 to 10 less concentration than the straight chain hydrocarbons.

The second fraction (fraction B) eluting from the HPLC was the most complex of the major fuel fractions. GC/MS identification indicated that the major constituents in the fraction were alkyl substituted benzene compounds (C₄-C₁₁ benzenes). Because of the great number of positional isomers, it was not possible to thoroughly assign specific structural identities to the constituents. Rather, individual compounds were identified as the number of carbon substitutions on the benzene rings. Some of the constituents in this fraction are identified in Figure 8. Note that several straight chain, saturated hydrocarbons have been identified in fraction B. These are present because of an incomplete resolution between fractions A and B. The approximate quantities of some of the selected constituents are reported in Table 5.

The third fraction eluting from the HPLC is composed predominantly of two-ring aromatics, including naphthene, alkylated naphthenes, alkylated biphenyls, and small amounts of thiophenes. Major constituents of the fraction are identified in Figure 9. In Table 6 a list of the values for the concentrations of the methyl, dimethyl, and trimethyl substituted naphthalenes in the fuel fraction C is presented. Concentrations of the substituted naphthalenes ranged up to approximately 11 milligrams per gram.

TABLE 5. CONCENTRATIONS OF SELECTED CONSTITUENTS
ONE-RING FRACTION OF DIESEL FUEL

Constituent	Retention Time, Min ^a	Concentration (mg/g fuel, mean \pm one standard dev)
C ₄ -Benzene	19.1	2.5 \pm 0.3
C ₅ -Benzene	30.1	1.8 \pm 0.2
C ₆ -Benzene	37.6	1.2 \pm 0.2
C ₇ -Benzene	41.5	1.0 \pm 0.2
C ₈ -Benzene	50.2	1.2 \pm 0.4
C ₈ -Benzene	52.4	0.5 \pm 0.3

^aSee Figure 8

TABLE 6. CONCENTRATIONS OF SELECTED CONSTITUENTS
TWO-RING FRACTION OF DIESEL FUEL

Constituent	Retention Time, Min ^a	Concentration (mg/g fuel, mean \pm one standard dev)
Naphthalene	31.3	1.3 \pm 0.5
Methyl Naphthalene	39.2	9.1 \pm 1.2
Methyl Naphthalene	40.3	5.7 \pm 0.8
C ₂ Naphthalene	46.1	4.7 \pm 0.8
C ₂ Naphthalene	46.9	4.8 \pm 0.9
C ₂ Naphthalene	47.8	11.0 \pm 1.8
C ₂ Naphthalene	49.0	5.8 \pm 1.5
C ₃ Naphthalene	56.3	2.9 \pm 0.5
C ₃ Naphthalene	57.1	3.1 \pm 0.3

^aSee Figure 9

Figure 10 is a high resolution gas chromatogram of the D fraction of the diesel fuel. Major constituents in this fraction include fluorene, alkylated fluorenes, phenanthrene, and alkylated phenanthrenes. Traces of multi-substituted alkyl naphthalenes were also present due to the incomplete resolution of fractions C and D of the fuel. In Table 7 the concentration of some selected compounds in fraction D are listed. In this case, phenanthrene was present in the highest concentration: approximately 4.9 micrograms per milligram fuel.

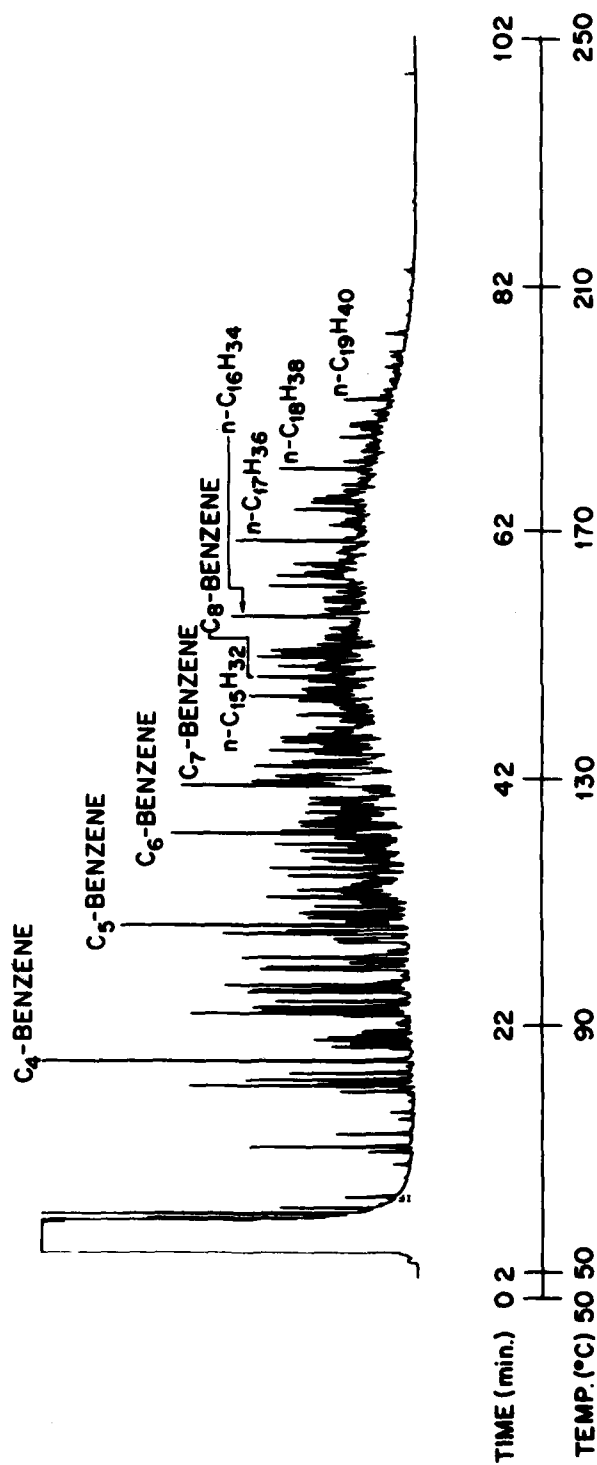


Figure 8. High Resolution GC Profile of the One-Ring Fraction of Diesel Fuel

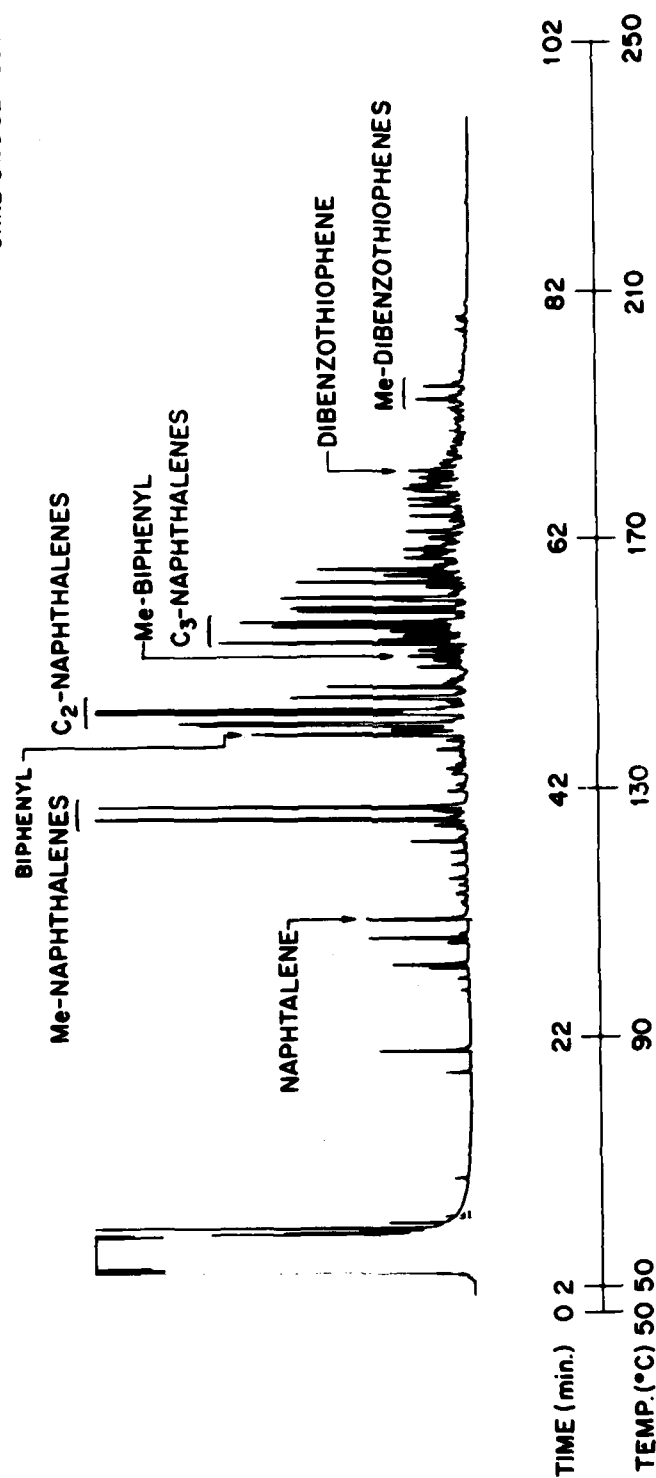


Figure 9. High Resolution GC Profile of the Two-Ring Fraction of Diesel Fuel

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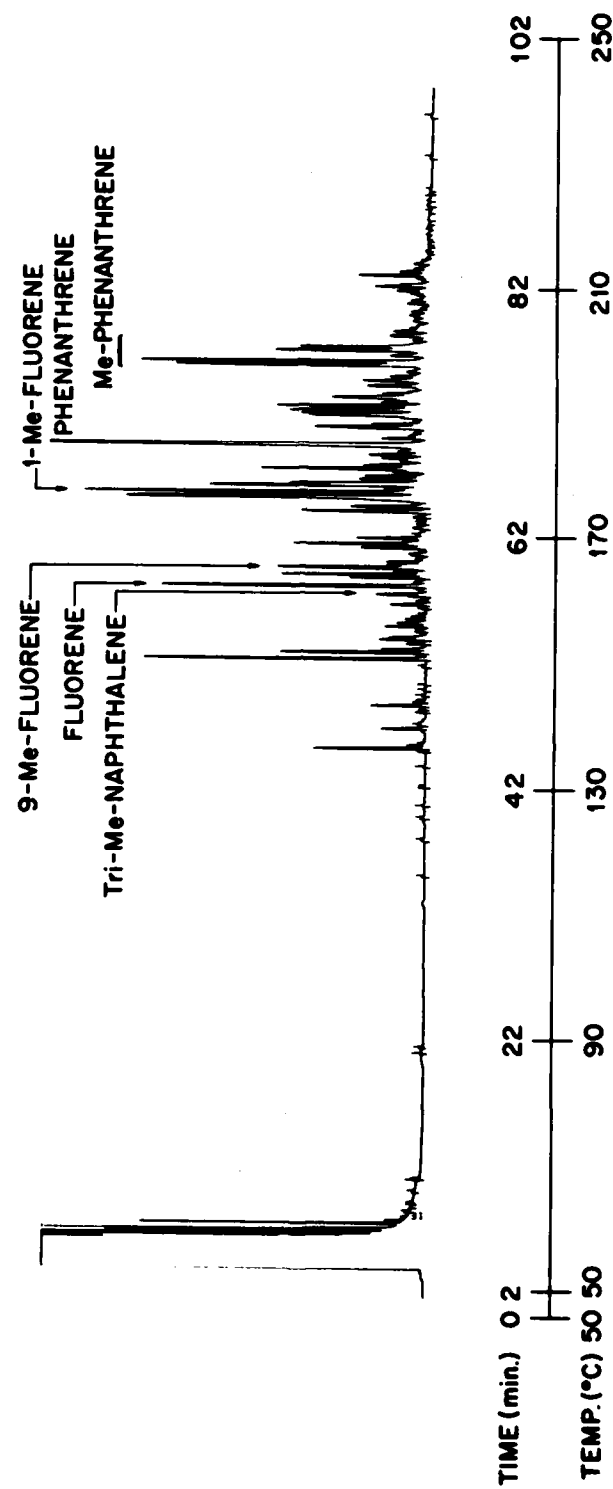


Figure 10. High Resolution GC Profile of the Three-Ring Fraction of Diesel Fuel

TABLE 7. CONCENTRATIONS OF SELECTED CONSTITUENTS
"THREE-RING" FRACTION OF DIESEL FUEL

Constituent	Retention Time, Min ^a	Concentration (mg/g fuel, mean \pm one standard dev)
Tri-Methyl Naphthalene	56.3	0.4 \pm 0.4
Fluorene	57.7	1.0 \pm 0.3
1-Methyl Fluorene	65.1	2.6 \pm 0.4
Phenanthrene	68.9	4.9 \pm 0.7
Methyl Phenanthrene	75.5	3.1 \pm 0.5

^aSee Figure 10

Changing the mobile phase to methylene chloride (or 50:50 MeCl₂: hexane) resulted in the elution of a fifth, or semi-polar fraction, from the HPLC column. A high resolution gas chromatogram of this fraction, which comprised approximately 0.2 percent of the total weight of the fuel, is portrayed in Figure 11. Ammonia chemical ionization mass spectrometry was used to determine that the major constituents of this fraction were alkyl substituted indoles, carbazole and alkyl-substituted carbazoles. Semi-quantitative analysis of the individual constituents of this fraction (Table 8) indicated levels up to 30 micrograms per gram fuel (ppm) for the substituted indoles, approximately 90 ppm for the carbazole, and as much as 40 ppm for the alkyl-substituted carbazoles. The relative proportion of the total fuel that this particular fraction represented was determined in much the same way that

TABLE 8. CONCENTRATIONS OF SELECTED CONSTITUENTS IN THE
SEMI-POLAR FRACTION OF DIESEL FUEL

Constituent	Retention Time, Min ^a	Concentration (μ g/g fuel, mean \pm one standard dev)
C ₁ -Indole	45.3	21 \pm 6
C ₂ -Indole	49.9	27 \pm 10
C ₃ -Indole	57.5	12 \pm 7
Carbazole	71.6	93 \pm 16
C ₁ -Carbazole	76.0	28 \pm 17
C ₂ -Carbazole	78.3	40 \pm 6

^aSee Figure

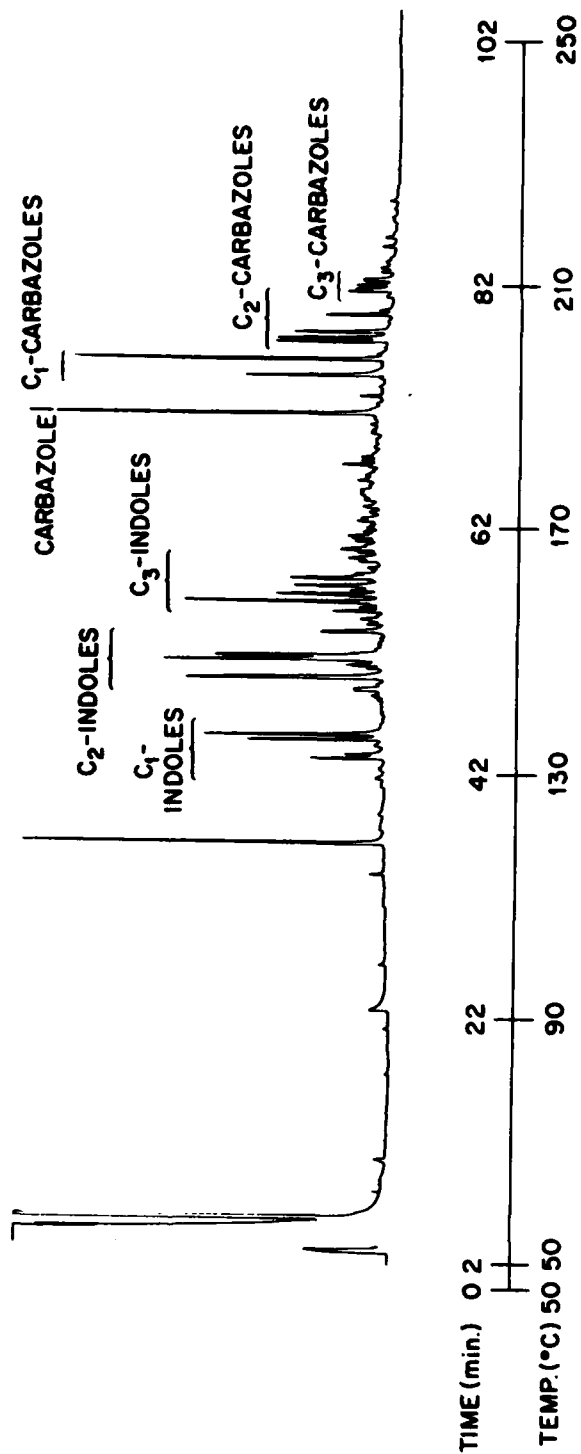


Figure 11. High Resolution GC Profile of the Semi-Polar Fraction of Diesel Fuel

the aromatics/aliphatics ratio was determined for the bulk of the fuel. That is, the area ratio of the particular fraction to that of the known weight of compounds which were major constituents of that fraction was determined.

BaP analyses of the diesel fuels used in these studies yielded values of 41, 102, and 72 nanograms per ml fuel. The average level of 72 nanograms per mL is similar to, but somewhat larger than, the average of 26 nanograms per milliliter which is reported in the Franklin Institute's literature review of diesel fuel toxicity.⁴ The 72 nanogram per mL average is considerably lower than the 1-5 micrograms per mL typically found in petroleum crude oils.²

We had noted on several occasions that the diesel fuel tended to darken with intermittent exposure to room air and light. In order to systematically study the phenomenon and determine its potential effect on the chemical composition of the fuel, refrigerated fuel was removed from storage, aliquoted into clear glass bottles, and stored under a variety of conditions. These included (a) refrigeration at 4°C, in the dark, (b) room temperature storage in the dark, (c) room temperature storage and exposure to laboratory levels of light and (d) room temperature storage with exposure to laboratory light and air. Periodically, samples of the stored fuel were subjected to a battery of analytical procedures, including high resolution gas chromatography, UV/ visible spectrophotometry, simulated distillation, viscosity, and nondispersive FTIR. Essentially, the only procedure which was capable of discriminating among the various storage conditions was the spectrophotometry. Results of these analyses are reported in Table 9. The data indicate that exposure to room light seems to have the greatest effect on the color of the fuel. This was confirmed by visual observation. During the first 3 months of exposure to light, absorbance at 460 nm increased steadily. This was followed by a significant decrease. We noted that

TABLE 9. EFFECTS OF STORAGE CONDITIONS ON DIESEL FUEL "AGING"
ABSORBANCE OF NEAT FUEL AT 460 NM

Elapsed Time, days	Conditions			
	A 4°, Dark	B 23°C, Dark	C 23°C, Light	D 23°C, Light, Air
0	.345	.345	.345	.345
15	.360	.370	.570	.600
29	.328	.404	.646	.700
50	.330	.425	.920	.900
85	.334	.480	1.43	1.12
123	.373	.560	.925	1.18
192	.336	.460	.820	.890

during the course of the tests a dark amber, waxy sediment formed in the bottles exposed to light. We speculate that the rise and subsequent decrease in absorbance was partially due to formation of the amber substance in suspension in the fuel, followed by its eventual precipitation. The source of the color change is unknown, but we have noted that solutions of indole standards tend to turn yellow with continued exposure to light.

PHYSICAL CHARACTERIZATION OF THE DIESEL FUEL SMOKE:
PARTICLE SIZE DISTRIBUTION

INTRODUCTION

It is well accepted that the pattern of aerosol deposition in the respiratory system of animals is a function of the sizes of the particles inhaled and that the size and point of deposition may influence toxicological results. Particle size distributions are not only dependent on the method of generation, but also on the time elapsed from formation to sampling, with the rate of growth being concentration-dependent. The diesel fuel aerosol has been studied at sufficiently high concentrations so that it was to be expected that particle sizes would change appreciably as a function of chamber concentration. In this section, the results that were obtained in the toxicology chambers both with and without animals present are reported.

METHODS

The results presented here were all obtained by cascade impaction techniques. A simple seven stage impactor of Mercer/Lovelace design⁵ was used. Each stage has a single cylindrical jet. The aerosol impinges on glass microscope cover slips where it is collected for analysis. Particles escaping the final stage were collected on a small glass-fiber 'absolute' filter. The impactor was designed for flow rates of one liter per minute. Uniform flows were maintained using flow-controlled sampling pumps set at 1.00 L/m. These pumps were frequently calibrated using soap-bubble meters.

In the course of this investigation two techniques were used to measure the amount of diesel fuel that was collected on each stage. Most used was a chromatographic technique. Immediately after sampling, each glass stage plate and the filter were transferred to small glass bottles. A known amount (usually 2 mL) of carbon disulfide was added to dissolve the fuel particulates. A small aliquot (10 μ L) was injected into a short chromatographic column operating at constant temperature. A flame ionization detector was used to detect the fuel vapors coming through the column. Chromatographic conditions are listed in Table 10.

The conditions were such that all of the components of the fuel passed through the system in about three minutes. The amount of fuel

TABLE 10. CONDITIONS FOR RAPID CHROMATOGRAPHIC ANALYSIS OF
DIESEL FUEL SMOKE PARTICLES FROM CASCADE IMPACTION STAGES

Column: 1/4" o.d. x 18" stainless steel packed with 5% SP 2100
on 100-120 mesh Supelcoport
Injector Temperature: 250°C
Detector and Temperature: Flame ionization at 350°C
Carrier Gas: Helium
Flow Rate: 40 mL per minute

particles in each solution (and hence on each stage) was determined by time integration of the signal. An LSI-11 MINC (Digital Equipment Co.) computer equipped with an analog-to-digital converter was used to collect and process the data. Occasionally, samples of pure diesel fuel at known concentrations were run to assess the sensitivity of the system, but it should be noted that only relative quantities were used in the impactor calculations of size and distribution. Carbon disulfide (CS₂) was used as a solvent because of its very weak flame ionization response. CS₂ response was separately measured for each run and these blank values were subtracted from sample responses.

The above technique was developed because of our inability to directly weigh the with sufficient precision the amount of fuel on each stage. Near the end of the investigation, it was found that, if the plates were properly cleaned and carefully handled, direct weighing could be accomplished to a precision of about 0.1 mg. With this precision, direct weighing was finally used rather than the more cumbersome chromatographic technique.

DATA REDUCTION

Cascade impactor stage constants have not been determined experimentally, but were calculated based on measured orifice diameters using the formalism developed by Marple⁶ and Marple and Liu.⁷ Each stage can be characterized by a dimensionless Stokes number (S) given by

$$S = \frac{\rho CVD^2}{9\mu W} \quad (1)$$

where ρ is the particle density (g/mL)
V is the air velocity through the orifice (cm/sec)
D is the (Stokes) particle diameter
 μ is the viscosity of air
W is the orifice diameter
and C is the Cunningham correction factor defined as

$$C = 1 + \frac{0.16}{DP} + \frac{0.055}{DP} \exp \left[-\frac{DP}{0.15} \right] \quad (2)$$

As shown by Marple, the collection efficiency curve for each stage need not be determined experimentally, but depends on the Stokes number of the stage. The 50 percent efficiency point for the stages comes at $S = 0.49$ for the cylindrical jet impactors used here.⁸ Noting that the volumetric flow rate Q is related to the air velocity and orifice diameter by

$$Q = \pi V W^2 / 4 \quad (3)$$

Eq. 1, rearranged, becomes

$$D_{50} \sqrt{C} = \sqrt{S_{50}} \left(\frac{9\pi W^3}{4\rho Q} \right)^{1/2} \quad (4)$$

where D_{50} is the diameter corresponding to the 50 percent collection efficiency point. With this assignment, all terms on the right are defined and one can calculate the 50 percent cutoff point for each stage (D_{50}) and C by graphical or iterative solutions of equations 2 and 4. For this work a BASIC program to solve them iteratively has been written (Appendix). Data for our impactor specific to diesel fuel aerosol of density = 0.87 g/mL and a flow rate of 1 liter per minute are contained in Table 11.

TABLE 11. STAGE CONSTANTS FOR CIRCULAR JET IMPACTORS

Flow Rate = 1000 mL/min.			Particle Density = 0.87 g/mL			
JET DIAMETERS		PRESSURE Atm.	STOKES		AERODYNAMIC	
In.	Cm.		Diam.	Cunn. Cor.	Diam.	Cunn. Cor.
0.930	0.2362	1.000	5.205	1.0307	4.850	1.0330
0.0700	0.1778	1.000	3.372	1.0475	3.140	1.0510
0.0560	0.1422	1.000	2.390	1.0669	2.224	1.0719
0.0480	0.1219	1.000	1.881	1.0851	1.749	1.0915
0.0380	0.0965	1.000	1.303	1.1228	1.210	1.1323
0.0270	0.0686	1.000	0.750	1.2137	0.695	1.2310
0.0170	0.0432	1.000	0.338	1.4899	0.311	1.5373

Particle size data reported here are summarized in terms of the mass median diameter and the geometric standard deviation for each run. An analysis of a typical run is shown in Table 12 and Figure 12 and are discussed to indicate the limitations of the method. The details of the stage analyses are shown in Table 12. In Figure 12, the cumulative percent of material less than a given diameter (column 6 of Table 12) is plotted using normal probability coordinates vs. the logarithm of the diameter (column 2). In this construct, a particle size distribution that is logarithmic-normal would plot as a straight line. The

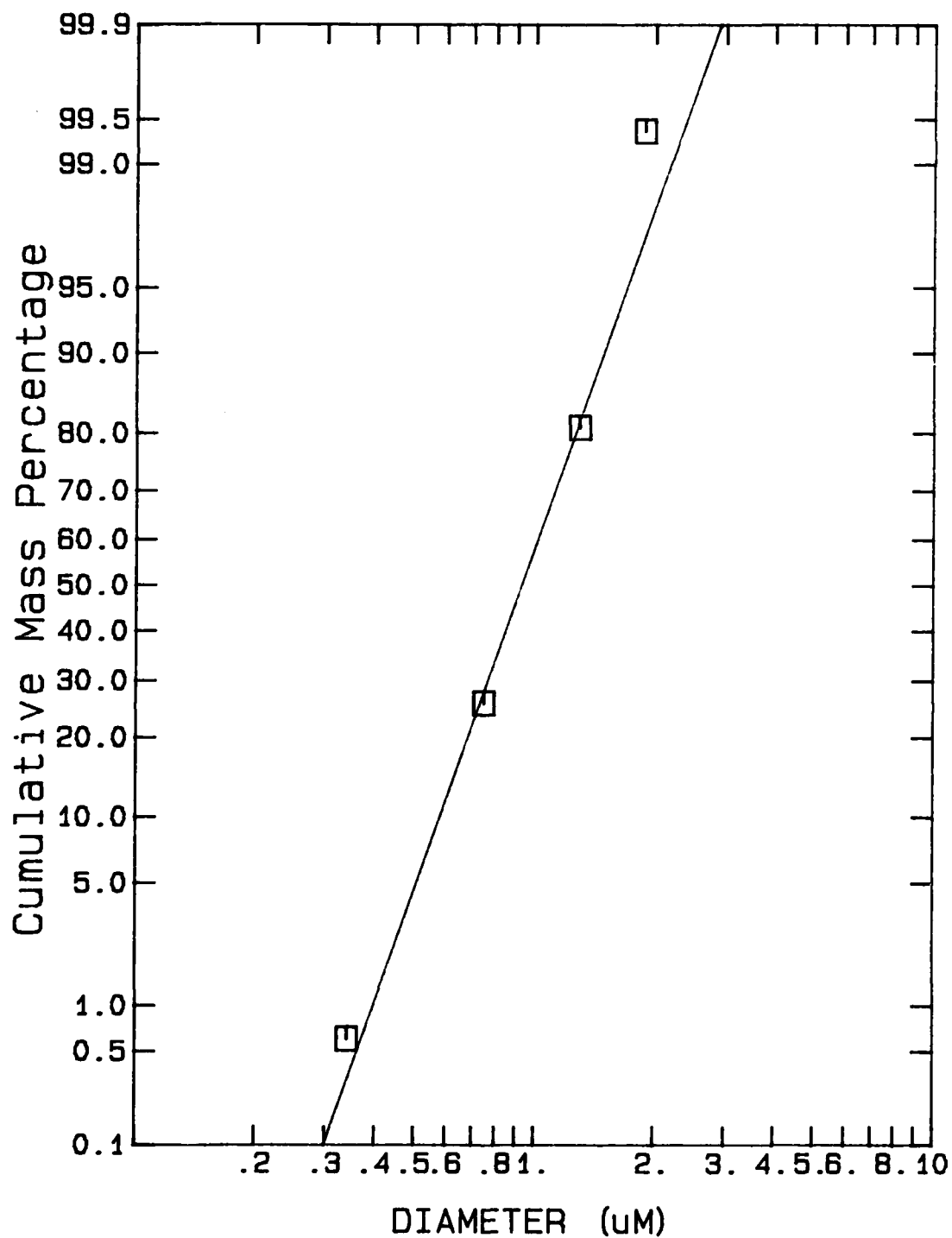


Figure 12. Log-Normal Plot of Particle Size Distribution from Typical Cascade Impactor Collection of Diesel Fuel Smoke

TABLE 12. PARTICLE SIZE DATA FROM TYPICAL CASCADE IMPACTOR RUN

Stage	Stage Diam ^a	Area ^b of GC Response	Area ^c -Blank	Percent ^d on each Stage	Wt. Percent of particles less than D
	μm	units	units	%	%
1	5.21	221	0	0	100
2	3.37	201	0	0	100
3	2.39	213	0	0	100
4	1.88	310	70	.6	99.4
5	1.30	2507	2277	18.6	80.8
6	0.75	6690	6760	55.1	25.7
7	0.34	3312	3082	25.1	.6
F	--	304	74	.6	

^aStage constants in μm from Table 11.

^bTotal area under GC response curve. Units are arbitrary.

^cArea after subtracting CS_2 blank response of 230. Proportional to amount of DF2 oil each stage. Approximate proportionality relation is: $\text{mg DF2} = \text{Area} \times 5 \times 10^{-4}$.

^dNote that total area of first three stages is less than measured blank response and is assigned as zero. This is a consequence of variability of experimental responses.

mass median diameter is the intercept of the 50 percent line (regardless of distribution type). The geometric standard deviation is calculated from the slope of the line. As can be seen from the table and figure, only three stages had appreciable amounts of material on them; the influence of the blank severely limited the precision to which amounts on other stages could be determined. Furthermore, these three data points translate to only two well determined points on the plot. Thus, cascade impaction techniques as used here give few reliable data as to the detailed shape of the distribution; we assume lognormality for simplicity of discussion. Valid data are obtained for the mass median diameters. The conclusions we draw from the example shown here are quite general for all of the data obtained. Fundamentally, it is a consequence of the low polydispersity (small geometric standard deviation) of aerosols of this type (see reference 9 for a discussion of similar highly concentrated condensation aerosol). The lower the polydispersity, the higher the resolution required to determine details of the distribution. This technique for estimating the mass median diameters is graphical, as indicated in Figure 12. A "best fit" straight line is drawn through the data points, subjectively weighting those points derived from stages containing larger amounts of material

most heavily. We thus interpolate the best data to the 50 percent mass point. The slope from which we derived the geometric standard deviation is perhaps more uncertain, but inasmuch as throughout the investigation we have seen no major deviations from a value of 1.4, the results are quite adequate for the intended purposes.

RESULTS AND DISCUSSION

The aerosol generation facilities and the chambers used for the toxicology studies have been previously described¹⁰, as have some of the inhalation toxicology experiments.¹¹ Particle size data taken from these chambers during the course of the toxicology study are tabulated in Table 13. Usually, impactor samples were taken from chamber ports just above the top shelf of animal cages (top) and just below the bottom shelf (bottom). It can be noted from Table 13 that the particle diameters at the bottom port are usually slightly greater (ca. 0.2 μ m) than at the top. This is a consequence of particle growth and is particularly evident at the higher concentrations. The aerosol is flowing through the chambers approximately laminarly.¹⁰ The chamber volume subtended by the sampling ports was approximately one cubic meter. At the volumetric flow rate used (420 L/min), two and one-half minutes are required for the aerosol to flow from top to bottom. This time is sufficiently long that some coagulation growth is to be expected.

The chamber particle size data are summarized in Figure 13, where the averages of the top and bottom measurements are plotted against the aerosol concentration. An arbitrary straight line has been drawn through the points to emphasize the trend toward increased size with concentration. Particle growth theory would certainly predict a non-linear curve, but, in view of the data scatter, no attempt has been made to refine the curve. Points are plotted distinguishing size measurements in chambers with and without the presence of animals. It can be seen that no large or significant difference in size distribution was seen in chambers with or without animals present.

CHEMICAL CHARACTERIZATION OF THE DIESEL FUEL SMOKE

INTRODUCTION

The generation of the diesel fuel smoke for this study has been described elsewhere.¹⁰ Briefly, the diesel fuel is injected onto a Vycor glass heater held at 600°C. The vaporized fuel is then swept into a stream of air with nitrogen carrier gas. Upon contacting the cooler dilution air, the diesel fuel condenses and forms the smoke cloud, which is in turn swept into an animal exposure chamber. The single greatest effect of the high temperature aerosolization procedure is to partition the components of the diesel fuel between the vapor and liquid phases. Because the smoke is relatively concentrated and present as a two phase (liquid and vapor) system, the sampling and

TABLE 13. PARTICLE SIZE SUMMARY OF DF2 AEROSOLS IN EXPOSURE CHAMBERS

Date	Chamber Number	Conditions	Port	Concentration (mg/L)	Mass Median Diameter (μm)	Geometric Standard Deviation
02/24/81	34	empty chamber	top bottom	1.2 1.1	0.73 0.89	1.6 1.4
03/15/81	33	48 Rats	top bottom top bottom	1.4 1.3 1.4 1.1	1.03 1.03 1.07 0.90	1.4 1.4 1.4 1.4
03/23/81	33	48 Rats	top bottom top bottom	1.4 1.6 1.3 1.5	0.95 1.06 0.98 1.01	1.4 1.4 1.4 1.4
04/08/81	33	45 cases only	top bottom top bottom	1.4 1.5 1.2 1.2	0.78 1.02 0.80 1.12	1.3 1.4 1.3 1.4
05/19/81	34	44 Rats	top bottom	2.0 1.7	0.77 0.97	1.4 1.4
07/10/83	34	24 Rats	top bottom top bottom	6.0 6.3 6.4 6.3	1.76 1.86 1.67 1.91	1.3 1.4 1.3 1.3

TABLE 13. (Cont'd)

Date	Chamber Number	Conditions	Port	Concentration (mg/L)	Mass Median Diameter (μ m)	Geometric Standard Deviation
08/13/81	34	empty	top bottom top bottom top bottom	1.9 2.0 4.2 4.3 6.2 7.3	0.95 1.13 1.17 1.30 1.39 1.61	1.4 1.6 1.5 1.3 1.2 1.3
09/09/81	32	48 Rats	top bottom	2.1 1.9	0.99 0.97	1.4 1.4
10/04/82	32	48 Rats	top bottom	0.25 0.25	0.48 0.60	1.5 1.5
10/04/82	33	48 Rats	top bottom	0.75 0.75	0.54 0.64	1.5 1.5
10/04/82	34	48 Rats	top bottom	1.5 1.5	0.60 0.80	1.6 1.5

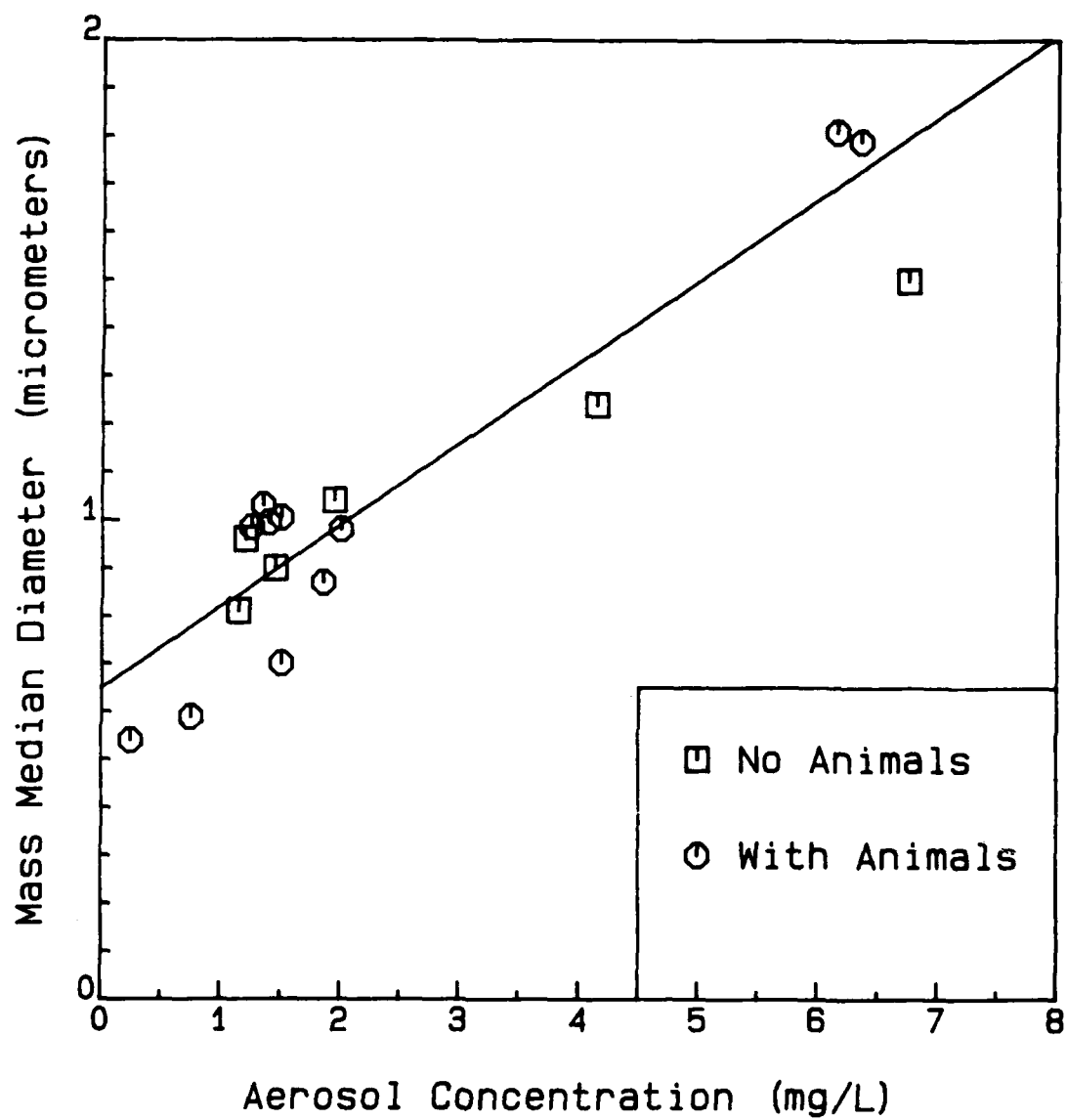


Figure 13. Particle Sizes of Diesel Fuel Smoke in Inhalation Exposure Chambers

analytical procedures must be designed such that the distribution of the chemical constituents between the two phases is not altered significantly.

METHODS

Samples of the diesel fuel smoke particle phase were collected on standard 45-mm Cambridge glass fiber filter pads¹² by drawing a known volume of the smoke through the pad with constant flow sampling pumps. The weight gain of the filter pad was then related to the volume of sample as the weight of smoke particulates per unit volume. Sampling flows of 2 L per minute or less were employed to minimize possible evaporation of collected particles or reentrainment of those particles into the sampling stream.

Because of the limited capacity of the adsorptive resins, sampling of the diesel fuel smoke for vapor phase constituents had to be performed somewhat differently than that for the particle phase sampling. In the former case, approximately 30 cc of the filtered smoke vapor was drawn with either a hand syringe or an infusion pump very slowly (1 cc per minute) through a glass tube containing 1.8 mL of Tenax GC®. For analysis, the Tenax® was desorbed at 250°C with helium purging for 10 min onto a nickel capillary precolumn cooled in liquid nitrogen. The precolumn was then attached to the primary GC column (60 m OV-101-coated glass capillary) and chromatographed by removing the liquid nitrogen and temperature-programming from 50°C to 180°C at 2° per minute.

Depending on the particular analytical scheme, particle phase samples were extracted from the Cambridge filter pads with either "distilled-in-glass" grade hexane or methylene chloride. The extracts were then reduced in volume to approximately 500 microliters and handled in much the same way as the fuel samples described above for HPLC and GC analysis.

Decachlorobiphenyl (DCBP) was determined gas chromatographically with electron capture detection on a 1 m x 6 mm o.d. 10 percent OV-1 on 80-100 mesh Chromosorb G-HP column. Column temperature was 220°, injector temperature was 250°, the detector was held at 300°.

One method of determining quantities of whole smoke or vapor phase in a given volume of smoke involved drawing a known amount of smoke into an evacuated 300-cc bulb. If vapor phase analysis was to be performed, the smoke was filtered immediately upstream of the bulb. For whole smoke analysis, the smoke was drawn, unfiltered, directly into the bulb. Next, 5 mL of carbon disulfide (CS₂) solvent was added to the bulb in order to dissolve the smoke constituents. After chilling of the bulb in a freezer (to aid in dissolution of smoke vapors into the CS₂), the bulb was warmed to room temperature. The carbon disulfide solution was removed and an aliquot injected into the GC. The same quantitation procedures used to determine the particulates

collected on the cascade impactor stages (see above) were used to determine the amount of smoke present in the bulb.

Another method for determining the quantity of vapor phase in a given smoke volume employed carbon molecular sieves. Personal air sampling pumps calibrated to operate at low flow rates were used to pull one-liter volume samples over a 7- to 12-minute time interval. Cambridge holders and filters, used to trap the particulate phase, were placed directly in the chamber to assure temperature equilibration and prevent condensation of species of the vapor phase prior to the vapor traps. One-fourth-inch o.d. x three-inch-long cartridges containing 175 mg Sphero carb®, a carbon molecular sieve, were used to collect the vapor phase. This material has been previously shown to retain low molecular weight constituents. Some samples were drawn with cartridges in series to assure that that breakthrough did not occur. Following collection, the vapor phase constituents were thermally desorbed from the cartridges at 350°C in the injection port of a gas chromatograph and re trapped in a precolumn immersed in liquid N₂. The precolumn served to introduce the sample as a narrow plug onto the analytical column which minimized peak broadening and facilitated quantitation. Since an estimate of the total vapor phase concentration was desired, the sample was chromatographed on a low resolution column packed with uncoated glass beads. Peak areas were integrated and compared to those areas obtained from direct injection of a liquid "standard" onto Sphero carb® cartridges. The standard was a distilled fraction of diesel fuel taken up to 235°C at atmospheric pressure. This fraction was chosen because previous high resolution chromatograms of the vapor phase showed that tridecane was the highest boiling major hydrocarbon present in the vapor phase.

Carbonyls in whole smoke were determined by the method of Manning and Maskarinec.¹³ Carbon monoxide (CO) determinations were made with an electrochemical CO analyzer (Ecolyzer, Energetics Sciences, Inc.). In order to perform carbon monoxide analyses on filtered smoke, it was necessary to remove organic vapor phase constituents, which interfered with the analysis, from the smoke. This was accomplished by adding a small glass tube, containing approximately 2 cc of Tenax® and 2 cc of activated charcoal, upstream of the Ecolyzer. Oxides of nitrogen (NO_x) analyses were performed by means of a Beckman Model 951 NO_x Chemiluminescent Analyzer using the same organic vapor trap as that used for the CO analyses. Determination of constituents in the nitrogen carrier gas was performed by mass spectrometry. Hydrogen cyanide in the whole smoke was determined by collecting the smoke on a Cambridge filter backed by a silica gel trap. The filter and trap were combined and analyzed according to the method of Collins et al.¹⁴

RESULTS AND DISCUSSION

Analysis of the nitrogen carrier gas used to generate the smoke aerosol was performed in order to insure that a significant amount of

the fuel would not be combusted by traces of oxygen present in the carrier gas during the aerosolization process. Results of the carrier gas analyses are found in Table 14. The data indicate only very minor traces of other gaseous constituents present in the carrier gas. Judging from the level of oxygen, very little combustion of the diesel fuel constituents would be expected.

TABLE 14. ANALYSIS OF NITROGEN CARRIER GAS USED FOR ANIMAL EXPOSURES

Compound	Weight Fraction*(%)
H ₂	0.0001
CH ₄	0.0007
H ₂ O	0.0011
N ₂ + CO	99.948
O ₂	0.0012
Ar	0.0483
CO ₂	0.0003

*Average of Duplicate Samples

Distribution of the Smoke Between Vapor and Particulate States

The obscurant cloud generated is an evaporation/condensation aerosol which undergoes a large dilution simultaneously with condensation. Many of the more volatile constituents in the fuel have significant vapor pressures at ambient temperatures and thus partition themselves between the vapor and particle phases. Besides complicating the sampling of the aerosol (since the method of sampling the cloud can ultimately affect the relative composition of the sample obtained), the presence of a two-phase system can complicate the interpretation of the results, because the experimental animals are exposed to both the liquid and vapor phase of the aerosol. The primary method of administration of the more volatile constituents is via the vapor phase, while the less volatile constituents are administered to the animals in the particle phase. The distinction may have toxicological significance, since organic vapors could be distributed through the lung and absorbed in a manner different from that of particles. Thus, it was desirable to obtain some independent measure of the concentration of each of the two phases of the system. Estimation of the concentration of particles in the aerosol was relatively straightforward. That is, a specific volume of smoke was filtered (at low flows) and the weight increase of the filter pad taken to be the weight of particles per unit volume.

Determination of the quantity of the vapor phase was considerably more difficult: For a sample sufficiently large to be accurately

weighed, it was difficult to assure that 100 percent recovery of all vapor phase constituents had occurred. In addition, we found that instrumental measurement of the quantity of vapor phase posed substantial problems of standardization and sample dilution. Thus, we attempted to use chemical measures of the amount of fuel present as a vapor in the obscurant smoke. Over the course of the study, four approaches were tried. Two of the methods, more indirect in nature, measured the amount of fuel which does not re-condense following aerosolization. The other two methods measured directly the amount of material present in the vapor phase. None of the methods was without some experimental difficulties. However, the results, taken together, provide a good estimate of the amount of material in the vapor phase as a function of the aerosol particle concentration. The procedures and their results are described below.

Material Balance. In this procedure, the amount of fuel being pumped into the smoke generator was very carefully metered. Using an exact determination of the airflow into the chamber, a total mass of fuel per unit volume was calculated. When compared with a value for the smoke particle concentration per unit volume - determined by conventional means - the difference was taken to be the amount of fuel constituents present in the vapor phase. Results of these material balance calculations are presented in Table 15. These data indicate that, over a particle concentration range of 1.8 to 6.3 mg per liter, the fraction of the fuel which remains uncondensed varies from approximately 28 to 16 percent. Of course, these calculations assume complete collection of the sampled particulates. If chamber wall deposition, or evaporation of collected particles from the filter occur, the calculated vapor concentrations will be higher than those actually present.

Tracer Method. This approach was thought to provide a good estimate of the relative fraction of vapor phase constituents in the aerosol. The change in the apparent concentration of a "non-volatile" tracer - one which has an extremely low vapor pressure at ambient temperatures - in the liquid phase of the aerosol can be used to determine this fraction through the following expression.

$$F = \frac{V-1}{V}$$

where F = the fraction of the fuel remaining in the vapor phase
V = the ratio of the concentration of the tracer in the aerosol particle phase to that of the tracer in the original fuel = (T_{part})/(T_{fuel}).

The concentration of vapors, C_v, is given by

$$C_v = (V-1)C_p$$

where C_p is the volume concentration of the particles.

In this case, decachlorobiphenyl (DCBP) was chosen as the nonvolatile tracer. DCBP was used as a dosimetric tracer in another experiment to determine deposition of the diesel fuel aerosol in rats in the inhalation toxicology study. In our experiments, no evidence of

TABLE 15. SMOKE VAPOR PHASE CONCENTRATIONS ESTIMATED FROM MATERIAL BALANCE CALCULATIONS

Average Measured ^a Smoke Particle Concentration (mg per liter)	Estimated Whole Smoke ^b Concentration (mg per liter)	Calculated ^c Vapor Phase Concentration (mg per liter)	Fraction of Introduced Fuel Remaining Un-Condensed (Percent)
6.32	7.57	1.25	16.5
4.06	4.97	0.91	18.3
4.08	4.97	0.89	17.9
1.78	2.46	0.68	27.6
5.23	6.24	1.01	16.2
3.08	3.73	0.65	17.4
5.20	6.25	1.05	16.8

^aDetermined gravimetrically from Cambridge filter pads.

^bDetermined from quotient of fuel flow into smoke generator and air flow into exposure chamber.

^cDifference between estimated whole smoke concentration and measured smoke particle concentration.

measurable quantities of the DCBP in the vapor phase was found following aerosolization. Thus, it was assumed that all of the tracer added to the fuel was present in the particle phase of the smoke. The results of one set of experiments conducted in a small cylindrical chamber are presented in Table 16. Additional results for a larger chamber are in Table 17. The data from both experiments suggest that, as the smoke particle concentration increases, the fraction of fuel which remains uncondensed generally decreases. However, the overall amount of material in the vapor phase increases.

TABLE 16. DCBP* ENRICHMENT AND CALCULATED VAPOR PHASE CONCENTRATION AS A FUNCTION OF SMOKE PARTICLE CONCENTRATION CYLINDRICAL CHAMBER

Smoke Particle Concentration, Cp, mg·L ⁻¹	Fraction of Fuel ^b Remaining in Vapor Phase, Percent	$\frac{[\text{DCBP}]_{\text{Particles}}^{\text{a}}}{[\text{DCBP}]_{\text{Fuel}}}$	Vapor Phase Concentration, Cv ^c , (mg·L ⁻¹)
0.43	20	1.25 ± 0.03	.11
1.0	18	1.23 ± 0.04	.23
3.0	17	1.21 ± 0.06	.63
5.0	14	1.17 ± 0.05	.85
8.0	7	1.08 ± 0.03	.64

*Decachlorobiphenyl

^aRatio of DCBP concentration in particle phase of aerosol to that added to fuel prior to aerosolization.

^bSince DCBP transfers quantitatively to particle phase of the aerosol, the fraction of the fuel remaining in the vapor phase, F, is given by

$$F = \frac{V-1}{V} \text{ where } V = \frac{[\text{DCBP}]_{\text{particles}}}{[\text{DCBP}]_{\text{fuel}}}$$

^cCv = (V-1) Cp where Cp = Smoke particle concentration

Bulb Sampling. Attempts were made to determine the vapor phase concentration by making a difference measurement. That is, particle concentrations, determined by the conventional filter pad method, were compared with whole smoke (vapor + particles) concentrations, determined by the bulb sampling method described above. At nominal smoke particle concentrations of 4.2 mg·L⁻¹, whole smoke concentrations were determined to be approximately 5.2 mg·L⁻¹. This indicated that, at this particular smoke particle level, vapor phase constituents were about 1 mg·L⁻¹, or about 20 percent of the mass of smoke. These values were in good agreement with those obtained by the DCBP tracer method.

TABLE 17. DCBP* ENRICHMENT AND CALCULATED VAPOR PHASE CONCENTRATION
AS A FUNCTION OF SMOKE PARTICLE CONCENTRATION
X-10 CHAMBER

Smoke Particle Concentration, C_p , $\text{mg}\cdot\text{L}^{-1}$	Fraction of Fuel ^b Remaining in Vapor Phase, Percent	$\frac{[\text{DCBP}]_{\text{Particles}}^a}{[\text{DCBP}]_{\text{Fuel}}}$	Vapor Phase Concentration, C_v^c , ($\text{mg}\cdot\text{L}^{-1}$)
0.96	24	1.32	0.31
0.96	29	1.40	0.38
0.99	30	1.42	0.42
1.25	30	1.42	0.53
1.26	30	1.42	0.53
1.76	21	1.27	0.48
2.37	23	1.30	0.71
3.60	19	1.23	0.83
3.61	21	1.27	0.97
5.84	11	1.12	0.70
6.34	15	1.17	1.08
6.88	12	1.14	0.96

*Same *, a, b, c as Table 11.

However, the bulb sampling procedure was fraught with many experimental difficulties. Because of the relatively low levels of smoke present in the chamber, the carbon disulfide blank represented a substantial fraction (25 percent) of the total FID response to the smoke- CS_2 solutions. Because of the high variability of the blank, (± 20 percent relative), we felt that the bulb sampling method provided only a semi-quantitative measure of the amount of total smoke mass present in a given volume.

Carbon Molecular Sieve. For determinations of the vapor phase concentration at low smoke particle concentrations, the filtered smoke vapors were trapped on carbon molecular sieves and subjected to thermal desorption/low resolution GC (see above). Results of the experiments - for particle concentrations of $0.26 - 1.0 \text{ mg}\cdot\text{L}^{-1}$ - are presented in Table 18. The data indicate no clear trend with particle concentration in the fraction of the total smoke that exists as a vapor. The average value was approximately 12 percent, which was somewhat lower than that which would be suggested by the less direct tracer or material balance methods. Vapor phase concentrations varied from $0.03 \text{ mg}\cdot\text{L}^{-1}$ to $0.12 \text{ mg}\cdot\text{L}^{-1}$ over the particle concentration range studied.

The data from the tracer, material balance, and molecular sieve trapping methods are summarized graphically in Figure 14. Considering

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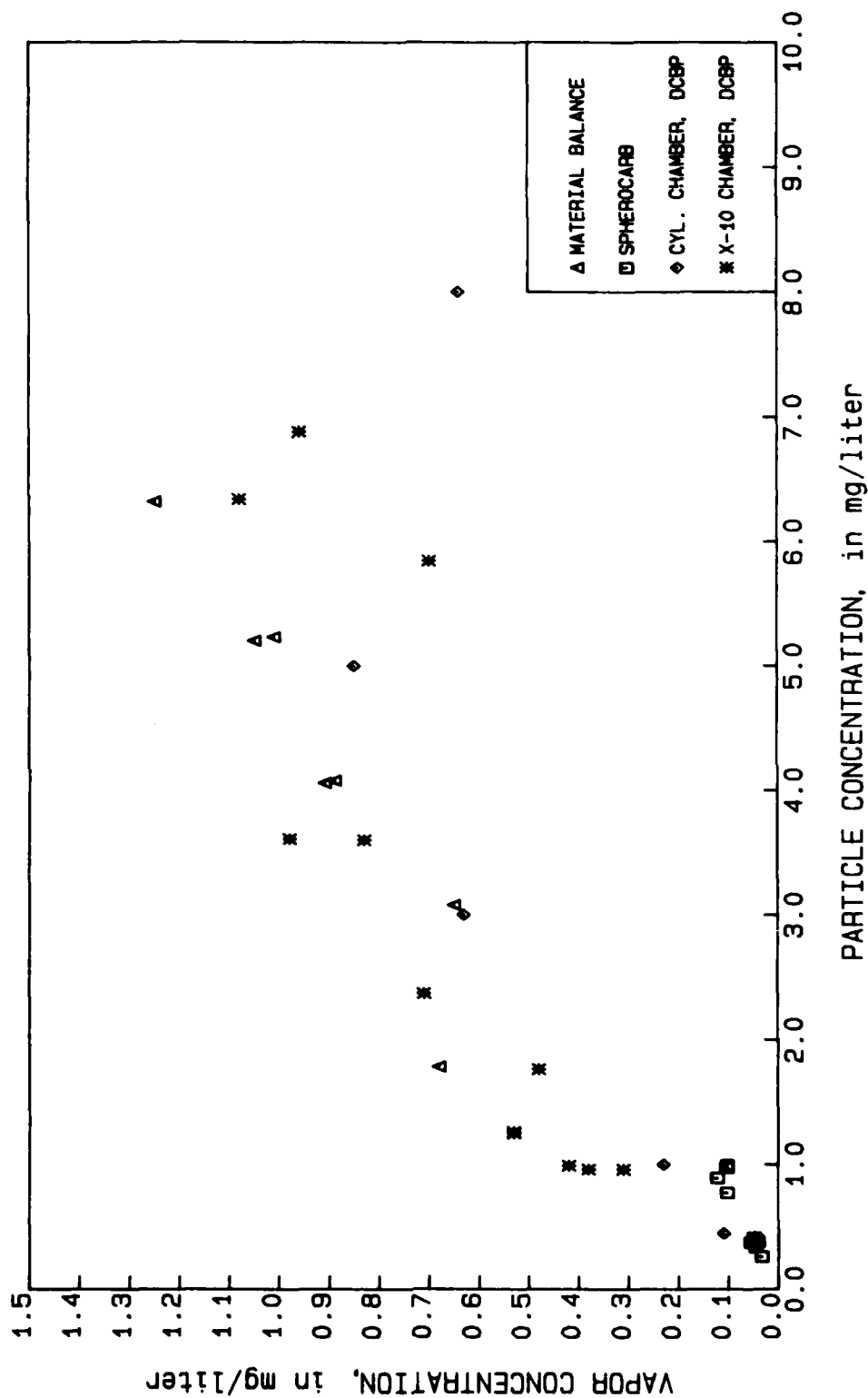


Figure 14. Vapor Phase Concentration of Diesel Fuel Smoke as a Function of Particle Concentration

TABLE 18. VAPOR PHASE CONCENTRATION AS A FUNCTION OF SMOKE PARTICLE CONCENTRATION AS DETERMINED BY CARBON MOLECULAR SIEVE (SPHEROCARB®) TRAPPING METHOD

Smoke Particle Concentration mg·L ⁻¹	Vapor Phase Concentration (mg·L ⁻¹)	Percent Vapor Phase
.262	.034	13.0
.338	.046	13.6
.376	.048	12.8
.376	.055	14.6
.377	.041	10.9
.395	.045	11.4
.414	.050	12.1
.891	.122	13.7
.772	.102	10.5
.972	.102	10.5
.972	.104	10.7
.995	.102	10.3
.995	.102	10.3

the differences in the methods, the data are relatively consistent. They show an increasing vapor concentration with increasing particle concentration. The rate of increase tends to diminish at higher particle concentrations, which might be intuitively expected.

Chemical Composition of the Diesel Fuel Smoke

The single most important effect of the aerosolization process on the fuel matrix is the partitioning of the fuel between a vapor and liquid phase. This is dramatically illustrated in Figure 15, which compares high resolution gas chromatograms of the unaerosolized fuel, the aerosol droplets collected on Cambridge filter pads, and vapors passing through the pad and adsorbed on Tenax-GC®. (Note that the lack of recovery of constituents boiling in the range of C₁₂ to C₁₄ was an artifact of the thermal desorption process and temperature program, and not an actual loss of the mid-boiling range constituents). In Figure 16, a more detailed comparison of the liquid phase of the smoke and the fuel - prior to aerosolization - is made. The loss of lower-boiling constituents in the liquid phase is a result of their higher vapor pressures at room temperature. When the fuel is heated and the vapors cooled, the more volatile constituents in the fuel do not condense as efficiently as the less volatile constituents.

In Tables 19-22 are listed the concentrations of selected constituents the aliphatic, the one-, two-, and three-ring fractions of the liquid phase of the smoke. Comparison of the data reported for the

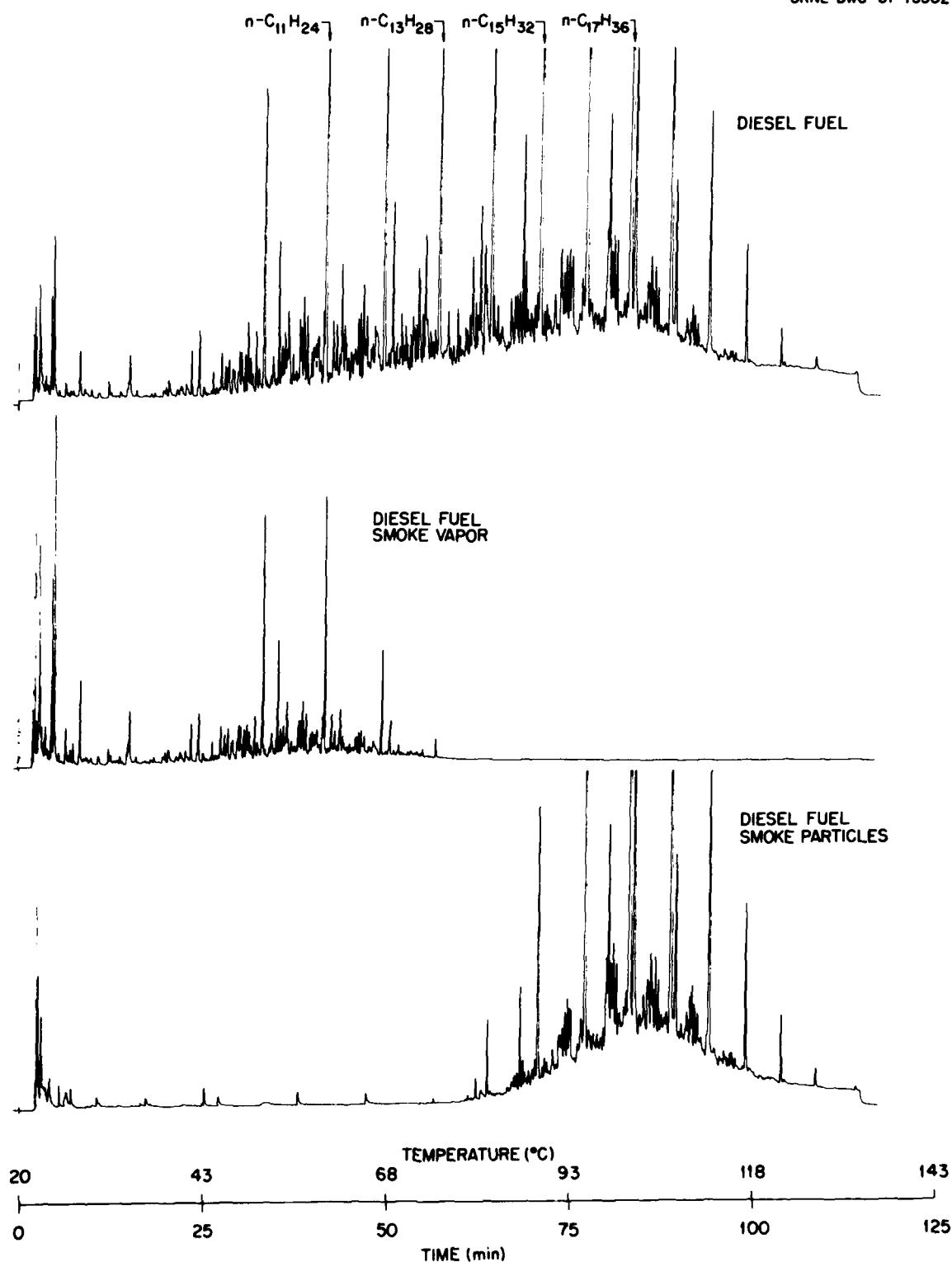


Figure 15. High Resolution GC Profiles: Fuel Prior to Aerosolization Compared to Smoke Vapor and Particle Phases

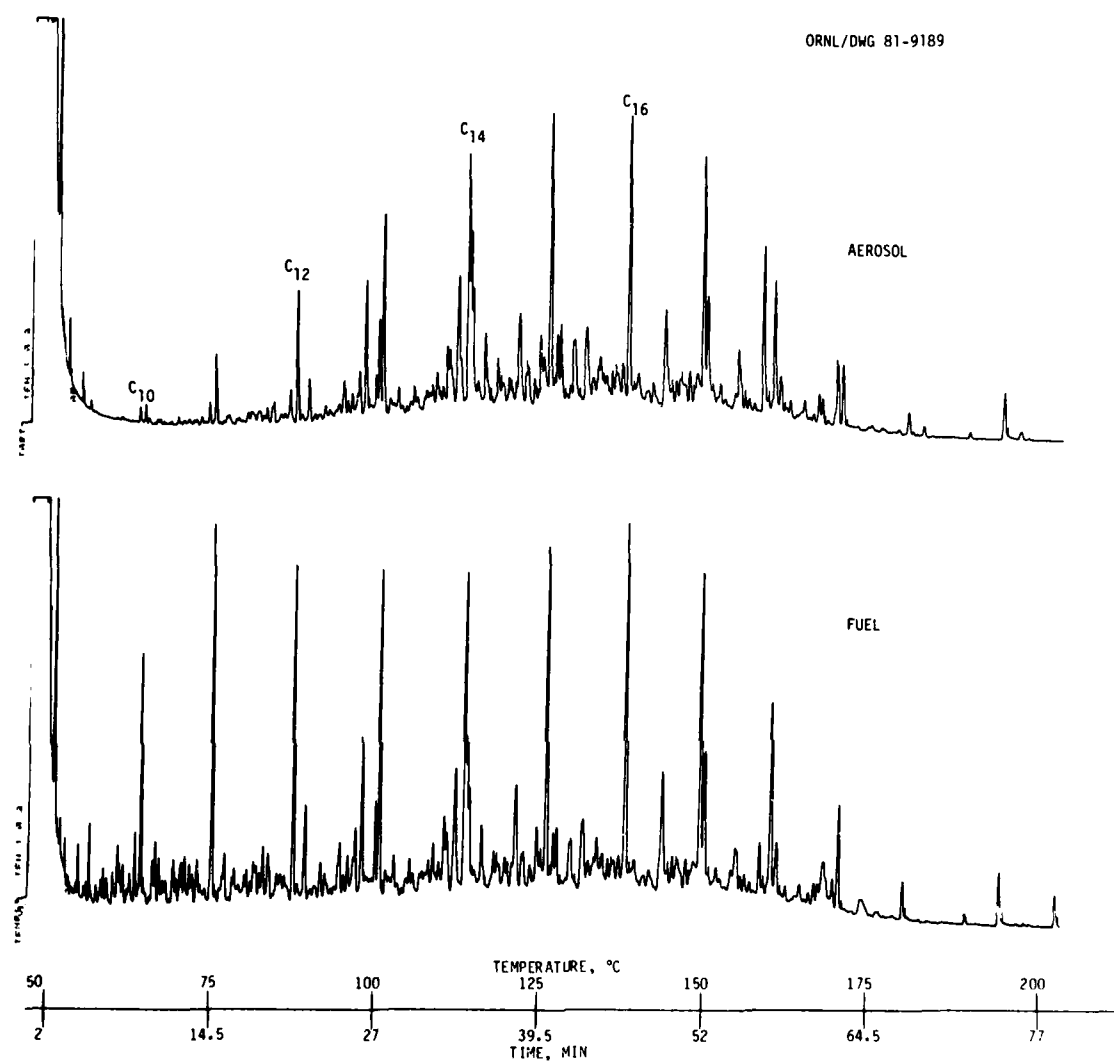


Figure 16. Comparison of High Resolution GC Profiles: Unaerosolized Diesel Fuel vs. Liquid Particle Phase Following Aerosolization

TABLE 19. CONCENTRATIONS OF SELECTED CONSTITUENTS
ALIPHATIC FRACTION OF THE LIQUID PHASE OF DIESEL FUEL SMOKE*

Constituent	Constituent Concentrations (mg/g smoke particulates, mean \pm one standard dev)
n-C ₉ H ₂₀	--
n-C ₁₀ H ₂₂	--
n-C ₁₁ H ₂₄	2.4 \pm 0.7
n-C ₁₂ H ₂₆	4.7 \pm 1.4
n-C ₁₃ H ₂₈	7.1 \pm 2.0
n-C ₁₄ H ₃₀	8.5 \pm 2.1
n-C ₁₅ H ₃₂	8.1 \pm 1.8
n-C ₁₇ H ₃₄	11 \pm 2.6
n-C ₁₇ H ₃₆	11 \pm 2.5
n-C ₁₈ H ₃₈	7.3 \pm 1.8
n-C ₁₉ H ₄₀	3.8 \pm 0.9
n-C ₂₀ H ₄₂	1.4 \pm 0.2

*Smoke Concentration: 5-6 mg/L

TABLE 20. CONCENTRATIONS OF SELECTED CONSTITUENTS
ONE-RING AROMATIC FRACTIONS OF THE LIQUID PHASE OF DIESEL FUEL SMOKE*

Constituent	Retention Time, Min	Constituent Concentrations (mg/g smoke particulates, mean \pm one standard dev)
C ₄ -Benzene	19.1	< 0.1
C ₅ -Benzene	30.1	0.4 \pm 0.1
C ₆ -Benzene	37.6	0.3 \pm 0.1
C ₇ -Benzene	41.5	0.4 \pm 0.1
C ₈ -Benzene	50.2	0.6 \pm 0.3
C ₉ -Benzene	52.4	--

*Smoke concentration: 5-6 mg/L

TABLE 21. CONCENTRATIONS OF SELECTED CONSTITUENTS
TWO-RING AROMATIC FRACTION OF THE LIQUID PHASE OF DIESEL FUEL SMOKE*

Constituent	Retention Time, Min	Constituent Concentrations (mg/g smoke particulates, mean \pm one standard dev)
Naphthalene	31.3	0.6 \pm 0.1
Methyl Naphthalene	39.2	7.4 \pm 1.9
Methyl Naphthalene	40.3	4.8 \pm 0.9
C ₂ Naphthalene	46.1	2.6 \pm 0.1
C ₂ Naphthalene	46.9	4.1 \pm 0.3
C ₂ Naphthalene	47.8	7.5 \pm 3.4
C ₂ Naphthalene	49.0	4.9 \pm 0.7
C ₃ Naphthalene	56.3	3.3 \pm 0.5
C ₃ Naphthalene	57.1	2.6 \pm 1.7

*Smoke concentration: 5-6 mg/L

TABLE 22. CONCENTRATIONS OF SELECTED CONSTITUENTS
"THREE-RING" AROMATIC FRACTION OF THE LIQUID PHASE
OF DIESEL FUEL SMOKE*

Constituent	Retention Time, Min	Constituent Concentrations (mg/g smoke particulates, mean \pm one standard dev)
Tri-Methyl Naphthalene	56.3	1.4 \pm 0.3
Fluorene	57.7	1.0 \pm 0.3
1-Methyl Fluorene	65.1	2.0 \pm 0.9
Phenanthrene	68.9	4.3 \pm 0.9
Methyl Phenanthrene	75.5	2.9 \pm 0.5

*Smoke concentration 5-6 mg/L

smoke particles with those reported for the fuel itself (Tables 4-8) indicates a lowered concentration of the one-ring aromatics and more volatile straight-chain hydrocarbons in the smoke particles. These are the types of constituents which would be expected to remain in the vapor phase as the fuel vapors condense to form the smoke. The concentrations of the other constituents in the fuel and smoke were generally within the range of experimental uncertainty of each other. In addition, no significant levels of constituents not present in the original fuel were observed in the liquid phase of the smoke.

Because of the volume reductions required to concentrate smoke particulate samples and the ensuing semi-polar fractions for high resolution GC analysis, it was not possible to obtain meaningful concentration values of the more volatile indoles and carbazoles in the smoke particles. However, GC profiles of the semi-polar fraction of the smoke particles did appear to be qualitatively similar to those of the unaerosolized fuel.

In Table 23 are listed the results of analyses for specific constituents which might be of toxicological importance in the diesel fuel smoke. No acrolein was detected, and hydrogen cyanide levels were indistinguishable from levels in the reagent blanks. Analyses for CO and NO_x were very difficult to perform, because of the interferences from organic vapor phase constituents in the smoke. There appeared to be a barely measurable amount of carbon monoxide present when apparent levels were corrected for vapor interferences. However, the actual CO level was thought to be much less than 1 ppm. NO_x content in the smoke was about 1 ppm. Acetaldehyde was the only measured constituent present in the smoke as a result of aerosolization (acetaldehyde content of the fuel was below detection limits). The acetaldehyde may arise from "combustion" of tiny amounts of the fuel with traces of oxygen in the carrier gas.

TABLE 23. EXPOSURE CHAMBER ATMOSPHERE : CONCENTRATION OF SPECIFIC CONSTITUENTS

Constituent	Concentration
Acetaldehyde	18 - 20 µg/L
Acetone	2 µg/L
Acrolein	Not detected
Carbon Monoxide	< 1 ppm
Hydrogen Cyanide	< 0.25 µg/L
Oxides of Nitrogen	1 ppm

^aDF smoke concentrations ranged from 3-5 mg/L

EFFECTS OF OXYGEN INCLUSION IN SMOKE GENERATOR CARRIER GAS

INTRODUCTION

Under field conditions, the VEES Smoke is generated in the exhaust manifold of a diesel engine. In contrast to the laboratory generated smoke, in which pure nitrogen is employed as a carrier gas, the field generator employs spent exhaust gases as the "carrier" gas. Among other substances, the exhaust gas contains a good deal of excess molecular oxygen (O_2), affording the opportunity for partial combustion of the injected diesel fuel and pyrosynthesis of new compounds. Thus, there exists some question as to the existence of toxicologically significant chemical differences between the smoke generated under field conditions and that being generated for bioassay. The discussion below attempts to address this issue. However, a concerted, detailed study of the effects of an oxygen-containing carrier gas on the chemical composition of the diesel fuel smoke was beyond the scope of this project. Rather, the results described below are a summary of observations made in the course of experiments either designed to investigate other phenomena, or to scope the problem in a limited fashion. Thus, the "conclusions" should be considered tentative and in need of additional verification and/or elucidation.

METHODS

For the limited scoping experiments, the diesel fuel smoke was generated with an oxygen-containing carrier gas. The gas consisted of nitrogen-breathing air mixtures to a maximum breathing-air level of 50 percent. The resulting 10.5 percent (by volume) oxygen concentration was designed to approximate that present in the exhaust gases of a diesel engine.

To determine the levels of CO and NO_x present in the oxygen-generated smoke, a chemiluminescent NO_x analyzer and an electrochemical carbon monoxide analyzer (Ecolyzer®) were employed. However, both of these systems respond to organic vapors. In addition, the Ecolyzer was shown to respond to NO_x with three times the sensitivity that it does to carbon monoxide. Some of the organic vapors could be eliminated by employing small vapor traps consisting of cartridges filled with Tenax® GC backed by activated charcoal. However, the traps had limited capacities and, at the sampling flow rates which had to be employed in the experiments, they tended to bleed organic vapors after a very short use. In addition, the inner surfaces of the CO and NO_x analyzers easily became contaminated with organic vapors. Compensation for these responses to the vapors was accomplished by alternate sampling of fresh air, smoke generated with nitrogen, and smoke generated with nitrogen and air -- all with known amounts of CO and/or NO_x added. The Ecolyzer® response to NO_x was corrected by independently measuring NO_x levels and subtracting them (corrected for sensitivity differences) from the Ecolyzer® readings. Other chromatographic methods employed were identical to those described above.

RESULTS

The most obvious effect of oxygenation is the distinct yellow color of the collected particulate matter. There was also an acrid odor which was not present with nitrogen-generated smoke. However, it was not possible to ascribe the observed color differences to any definite chemical change (see below).

From a compositional standpoint, the most discernable change was the increase in carbon monoxide concentration in the oxygenated smoke. Upon addition of air to the carrier gas, CO levels increased from less than 1 ppm to about 100 ppm (at smoke particle concentrations of 3-4 mg/L and breathing air fraction of 50%). NO_x levels increased from approximately 1 ppm to approximately 4 ppm.

In Figure 17 are compared an HPLC chromatogram of diesel fuel smoke (on an amino-silane column) generated with nitrogen carrier gas and that of a smoke generated with a 50-50 nitrogen/air mixture. Some differences in the chromatograms are readily apparent. First, there has been a substantial decrease in the amount of aliphatics (peak 1) when the 50/50 nitrogen/air mix is used. Secondly, there is a small increase in the peak height of peak 2 (peak 2 is thought to be predominantly comprised of one-ring aromatic compounds, but may include other volatile constituents of the diesel fuel smoke). Thirdly, there is a small additional peak which elutes prior to peak 2 which is much less prominent in a chromatogram of the smoke generated under a 100 percent nitrogen. These results suggest that the aliphatic constituents may be more susceptible to partial combustion than are the aromatic compounds.

In another set of experiments (described in detail in the Smoke Week III Report¹⁵), extracts of field generated (i.e., using battle tank exhaust) smoke particulates were subjected to high resolution gas chromatographic profiling. Comparison of the profiles with those obtained from the animal inhalation exposures (i.e., smoke generated with pure nitrogen carrier gas) indicated no major compositional differences which could not be ascribed to compositional differences between the two diesel fuels employed in the separate experiments. HPLC fractionation of the field generated particulates, followed by further high resolution gas chromatographic analysis, revealed no substantial compositional differences in the individual fractions.

DISCUSSION

Taken together, the results suggest that the field-generated smoke is likely to contain more CO and NO_x. However, these quantities are probably small in relation to the quantities of those compounds present in normal diesel exhaust. In addition, as much as 25-30 percent of the aliphatic constituents in the particle phase may be depleted due to combustion. That new compounds are synthesized when oxygen is added to the carrier gas is indicated by the change in color and odor of the smoke.

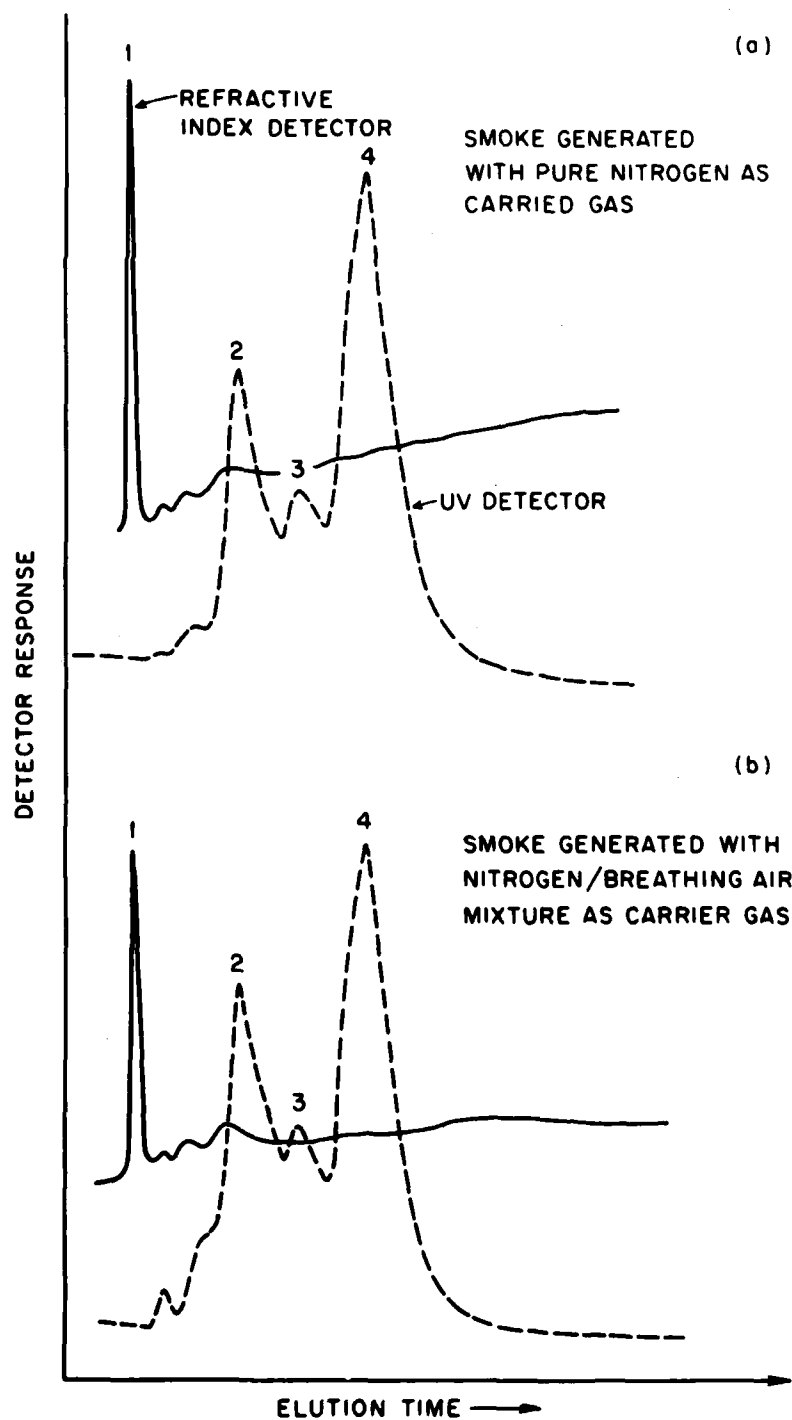


Figure 17. Comparison of HPLC Chromatograms: Smoke Particles Generated With Pure Nitrogen Carrier Gas vs. That Generated With 50:50 Air:Nitrogen Mixture

However, the HPLC and high resolution GC data suggest that the compounds are likely to be present in only very small quantities. The toxicological significance of these compounds is, of course, a matter of speculation.

LITERATURE CITED

1. Harmon, S. H. and J. E. Caton, "Diffuse Reflectance Infrared Fourier Transform Spectra of Selected Organic Compounds," ORNL/TM-8321, Available from NTIS, Springfield, VA, May 1982.
2. Tomkins, B. A., R. R. Reagan, J. E. Caton and W. H. Griest, "Liquid Chromatographic Determination of Benzo[a]pyrene in Natural, Synthetic, and Refined Crudes," Anal. Chem. 53, 1213-1217 (1981).
3. Buchanan, M. V., "Mass Spectral Characterization of Nitrogen-Containing Compounds with Ammonia Chemical Ionization," Anal. Chem. 54, 570-574 (1982).
4. Liss-Suter, D. and R. Mason, "Occupational Health and Safety Aspects of Diesel Fuel and White Smoke Generated From It," Final Report A056018, Franklin Institute Research Laboratories, Philadelphia, PA, DAMD-17-77-C-7020.
5. Mercer, T. T., M. I. Tillery, and C. W. Ballew. 1962. "A Cascade Impactor Operating at Low Volumetric Flow Rates," AEC Research and Development Report LF-5, December 1962. (The impactor was manufactured by In-Tox Products Co., Albuquerque, NM).
6. Marple, V. A., "Fundamental Study of Inertial Impactors," Ph.D. Thesis, University of Minnesota, Particle Technology Lab. Publication #144 (1970).
7. Marple, V. A. and Y. H. Liu, "Characteristics of Laminar Jet Impactors," Environ. Sci. and Technol. 8, 648 (1974).
8. Marple, V. A., Impactor Calculator, Sierra Instruments, inc., Carmel Valley, CA (1978).
9. Holmberg, R. W., "Determination of Particle Size in Tobacco Smoke Inhalation Exposure Devices Using Methylcyanoacrylate Fixation and Electron Microscopy," in "Tobacco Smoke Inhalation Bioassay Chemistry," M. R. Guerin, J. R. Stokely, and C. E. Higgins, Eds., ORNL-5424, Available from NTIS, Springfield, VA 22161.
10. Holmberg, R. W., J. H. Moneyhun, and T. M. Gayle, "Generating, Monitoring, and Controlling Petroleum Aerosols for Inhalation Chamber Studies," Task Summary Report, Oak Ridge National Laboratory, Oak Ridge, TN. ADA134214, ORNL/TM-8903.
11. Dalbey, W., and S. Lock, "Inhalation Toxicology of Diesel Fuel Obscurant Aerosol in Sprague-Dawley Rats," Final Report, Phase 1, Acute Exposures, Oak Ridge National Laboratory, Oak Ridge, TN. ADA132650, ORNL/TM-8867.

Literature Cited (Cont'd)

12. Wartman, W. B., E. C. Cogbill, and E. S. Harlow, "Determination of Particulate Matter in Concentrated Aerosols. Application to 'Tar' and Nicotine in Cigarette, Smoke," Anal. Chem. 31, 1705-1709 (1959).
13. Maskarinec, M. P., D. L. Manning, and P. Oldham, "Determination of Vapor Phase Carbonyls by High Pressure Liquid Chromatography," J. Liq. Chrom. 4, 31-39 (1970).
14. Collins, P. F., N. M. Sarji, and J. F. Williams, "An Automated Method for Determination of Hydrogen Cyanide in Cigarette Smoke," Tob. Sci. 14, 12-15 (1970).
15. Jenkins, R. A. and R. W. Holmberg. 1981. Appendix B: Chemical Sampling of VEES Smoke During Smoke Week III. UNCLASSIFIED. In Smoke Week III EO Systems Performance in Characterized Obscured Environment at Eglin AFB, FL, Aug 1980 (U). DRCPM-SMK-T-004-81. CONFIDENTIAL. ADC 026604.

APPENDIX

BASIC Computer Program for Iterative Calculation of Cut-off Diameters for Cascade Impactor Stages

```

10 REM Program IMPACT.BAS
15 REM Calculates stage constants for circular jet impactors

20 REM W0(I) = Jet diam. in inches; W1(I) in cm.
30 REM C0 = Cunningham corr. factor (Stokes)
35 REM C1 = Cunningham corr. factor (Aerodynamic)
40 REM S = Stokes 50% value.
50 REM V = Viscosity of air in poise
60 REM R = Density of particles (g/ml)
70 REM P(I) = Air pressure in atm. at each impactor stage
80 REM D0(I) = Stokes diameter for each stage
90 REM D1(I) = Aerodynamic diameter for each stage
100 REM Q = Volumetric flow rate thru impactor in ml/min.

110 REM set up initial values

120 DEF FNC(Y)=1+.16/Y+.055/Y*EXP(-Y/.15) : REM Cunningham eqn.
130 N=7 : REM the number of stages
135 REM Measured stage diameters (inches) in DATA statement
140 DATA .093,.070,.056,.048,.038,.027,.017
150 FOR I=0 TO N-1 : READ W0(I) : W1(I)=2.54*W0(I) : NEXT I
160 REM all pressures set to 1 atm. Can be changed in data state.
170 DATA 1,1,1,1,1,1,1
180 FOR I=0 TO N-1 : READ P(I) : NEXT I
190 S=.49*.49
200 V=1.81E-04

210 PRINT 'Volumetric flow rate (ml/min) ' ; : INPUT Q
220 PRINT 'Particle density (g/ml) ' ; : INPUT R
230 REM Calculate C0(I) and D(I)
240 X=SQR(S*9*PI*V*60/(4*R*Q))*10000
250 FOR I=0 TO N-1
260 P=P(I)
270 T=X*SQR(W1(I)*W1(I)*W1(I))*P
280 GOSUB 1000
290 C0(I)=C
300 D0(I)=Y1/P
310 REM Convert Stokes params to Aerodynamic
320 T=T*SQR(R)
330 GOSUB 1000
340 C1(I)=C
350 D1(I)=Y1/P
360 NEXT I

```

```

370 OPEN 'LP:' FOR OUTPUT AS FILE #1
380 PRINT #1, ' IMPACT.BAS'
390 PRINT #1,TAB(15);'STAGE CONSTANTS FOR CIRCULAR JET IMPACTORS'
400 PRINT #1,
410 PRINT #1,'FLOW RATE = ';Q;' ml/min.';TAB(40);'PARTICLE DENSITY=';
420 PRINT #1,R
430 PRINT #1,
440 PRINT #1,' JET DIAMETERS';TAB(21);'PRESSURE';TAB(31);' STOKES';
450 PRINT #1,TAB(51);' AERODYNAMIC'
460 PRINT #1,' inches';TAB(11);' cm.';TAB(21);' atm.';TAB(31);
470 PRINT #1,'Diam.';TAB(41);'Cunn. Cor';TAB(51);' Diam.';
480 PRINT #1,TAB(61);'Cunn. Cor.'
490 PRINT #1,'-----'
500 A$='#.#### #.#### #.#### #.#### #.#### #.#### #.####'
510 FOR I=0 TO N-1
520 PRINT #1,USING A$,W0(I),W1(I),P(I),D0(I),C0(I),D1(I),C1(I)
530 NEXT I
540 CLOSE #1
550 STOP

1000 REM Subr. to calc Cunningham factor iteratively
1010 Y=1 : REM initial guess of D*P
1020 C=FNC(Y) : REM est. of C based on Y
1030 Y1=T/SQR(C) : REM new approx. of D*P
1040 IF ABS(Y-Y1)<1.0E-06 THEN RETURN
1050 Y=Y1
1060 GO TO 1020

```

PERSONNEL

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R. A. Jenkins
R. W. Holmberg
M. R. Guerin
J. S. Wike
J. H. Moneyhun
P. Berlinski
B. E. Gill
R. S. Brazell
D. L. Manning

PUBLICATIONS

The following publications resulted in whole or in part from the work described in this report.

Jenkins, R. A. and J. S. Wike, "Chemical Characterization of Diesel Fuel Obscurants," Second Symposium on Physical and Chemical Characterization of Army Smokes/Obscurant Aerosols, Ft. Detrick, MD, November 13-14, 1980.

Dalbey, W. E., R. W. Holmberg, J. H. Moneyhun, R. A. Jenkins, S. Lock, and M. R. Guerin. Toxicological Evaluation of Diesel Fuel No. 2. Proc., 11th Conference on Environmental Toxicology, Dayton, OH, November 18-20, 1980.

Dalbey, W. E., S. Lock, R. W. Holmberg, J. H. Moneyhun, and M. R. Guerin. Acute Toxicity of an Aerosol of Diesel Fuel. Society of Toxicology Annual Conference, San Diego, CA, March 1-5, 1981.

Jenkins, R. A., R. W. Holmberg, J. H. Moneyhun, and J. S. Wike. Chemical and Physical Characterization of a Diesel Fuel Obscurant for Inhalation Toxicology Studies. Proc., Smoke/Obscurants Symposium V, Harry Diamond Laboratories, Adelphi, MD, April 28-30, 1981.

Dalbey, W. E., S. Lock, R. W. Holmberg, J. H. Moneyhun, and M. R. Guerin. Acute Exposure of Rats to an Inhaled Aerosol of Diesel Fuel. Proc., Smoke/Obscurants Symposium V, Harry Diamond Laboratories, Adelphi, MD, April 28-30, 1981.

Jenkins, R. A. and R. W. Holmberg. 1981. Appendix B: Chemical Sampling of VEESS Smoke During Smoke Week III. UNCLASSIFIED. In Smoke Week III EO Systems Performance in Characterized Obscured Environment at Eglin AFB, FL, Aug 1980 (U). DRCPM-SMK-T-004-81. CONFIDENTIAL. ADC 026604.

Jenkins, R. A., T. M. Gayle, J. S. Wike, and D. L. Manning. Sampling and Chemical Characterization of Concentrated Smokes. Toxic Materials in the Atmosphere, ASTM STP 786, American Society for Testing and Materials, 1982, pp. 153-166.

Jenkins, R. A., D. L. Manning, M. P. Maskariniec, J. H. Moneyhun, W. Dalbey, and S. Lock. Diesel Fuel Smoke Particulate Dosimetry in Sprague Dawley Rats. Task Summary Report to U.S. Army Medical Bioengineering Research and Development Laboratory, Ft. Detrick, Frederick, MD, 1983.

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